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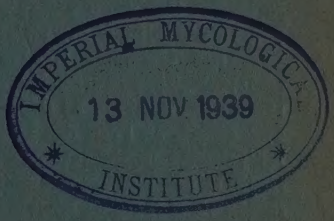

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MATHEMATICS

SOME NEW THEOREMS ON THE REPRESENTATION OF LARGE NUMBERS BY SEPARATE POSITIVE TERNARY QUADRATIC FORMS

By U. V. LINNIK

(Communicated by I. M. Vinogradow, Member of the Academy, 4. V. 1939)

The problem whether a positive ternary quadratic form $f(x, y, z)$ with integral coefficients and of invariants $[\Omega, \Delta]$ represents all sufficiently large numbers prime to $2\Omega\Delta$ and satisfying the generic conditions of $f(x, y, z)$ is still unsolved. In this direction I have proved the following theorems.

Theorem I. Let Ω be any uneven «quadratfrei» number. Denote by Γ the genus of positive ternary quadratic forms f_i of invariants $[\Omega, 1]$ with the following generic conditions: $\left(\frac{f_i}{\omega}\right) = \left(\frac{-1}{\omega}\right)$ for all $\frac{\omega}{\Omega}$; f_i do not represent the numbers $\equiv 7 \pmod 8$. Let a be any non-quadratic number. Then there exists a constant $C = C(\Omega, a)$ such that if a number m is $> C$, and both numbers m and am are prime to Ω and satisfy the generic conditions of Γ, then at least one of these numbers is primitively representable by all the forms f_i of Γ.

For instance: $\Omega = 1009; f = x^2 + 1009\,y^2 + 1009\,z^2$ for a suitably chosen constant C will represent at least one of the numbers m and $2m$ if $m > C$, $m \not\equiv 7 \pmod 8$ and $\left(\frac{m}{1009}\right) = +1$.

Theorem II. Every number $m > C(\Omega, \Delta)$ with $(m, 2\Omega\Delta) = 1$ satisfying the generic conditions of Γ is representable either by all forms of Γ or by all their reciprocals.

For instance, if $f = x^2 + 1009\,y^2 + 1009\,z^2$ and the number $m > C$ and satisfies the corresponding conditions, then either $m = x_1^2 + 1009\,y_1^2 + 1009\,z_1^2$ or $m = 1009\,x_2^2 + y_2^2 + z_2^2$.

Theorem III. If f is a form of the genus Γ and invariants $[\Omega, 1]$ or $[1, \Omega]$, then all numbers m which satisfy the corresponding generic conditions can be distributed into an infinite sequence of arithmetic progressions $\mathfrak{A}_i$ with the following property: for each $\mathfrak{A}_i$ we can choose a constant C_i such that if $m \in \mathfrak{A}_i$, $m > C_i$, then m is primitively representable by f.

The proofs of these theorems are rather long, and will be published elsewhere. I can only sketch here the principal features of the proof of theorem I.

If f is a form of the genus Γ and of invariants $[\Omega, 1]$, then the primitive equation $m_i = f(\xi, h, \zeta)$ can be written in the form

$$b + L = P \cdot X, \tag{1}$$

where b is a suitably chosen integer, L is a pure quaternion with the norm $-L^2=m_1$, P the «characteristic» integer quaternion of the form f with the norm Ω, X an integer quaternion. The number of solutions of the primitive equation

$$-L_i^2=x_i^2+y_i^2+z_i^2$$

is according to Siegel's recent result

$$>c_1 h(-m)>c_2(\varepsilon)\, m^{\frac{1}{2}-\varepsilon}.$$

We denote by τ the number $-\frac{\ln\left(1-\frac{1}{\Omega}\right)}{2\ln\Omega}>0$, by k the number $\left[\frac{8}{\tau}\right]+1$ and define s by the inequalities:

$$\Omega^s\leqslant m^{\frac{1}{4k}}<\Omega^{s+1}.$$

Then for all our L_i and for a suitably chosen b' (one and the same for all possible i) $i=1, 2, \ldots M$, we shall have

$$\left.\begin{array}{c} b'+L_i-P_{1i}P_{2i}\ldots P_{si}X_i;\quad \mathrm{Norm}\,(P_{ji})=\Omega \\ j=1, 2, \ldots s;\quad i=1, 2, \ldots M \end{array}\right\} \qquad (2)$$

If the number m_1 is not representable by the form f, then, as it may be easily shown, no one of the P_i can be equal to the «characteristic» quaternion P of the form f. This fact considerably reduces the total number of all possible different products $P_i=P_{1i}\ldots P_{si}$ $(i=1, \ldots M)$ in the equations (2).

Using de la Vallée Poussin-Landau's asymptotic laws of distribution of primes in progressions, the least possible number of different P_i in the equations (2) can be estimated for at least one of the cases: $m_1=m$ and $m_1=am$ (the numbers mentioned in the formulation). This estimation shows that for sufficiently large m (and consequently m_1), the fact mentioned above is impossible, so that f must represent either m, or am.

Theorem II is a rather simple consequence of theorem I, and theorem III is based on considerations analogous to that of I, with addition of Viggo Brun's sieve method. The theorem III is closely connected with.

Theorem IV. Let six numbers $\xi, \lambda, \zeta; \xi_1, \lambda_1, \zeta_1$ be given. If the congruence $\xi^2+\lambda^2+\zeta^2\equiv m \pmod{k}$ is satisfied for a given uneven integer k and simultaneously $\xi_1^2+\lambda_1^2+\zeta_1^2\equiv am \pmod{k}$, a being a given non-quadratic integer, then, for $m>C=C(a, k)$, at least one of the equations

$$x^2+y^2+z^2=m;\quad x\equiv\xi,\quad y\equiv\lambda,\quad z\equiv\zeta \pmod{k},$$
$$x_1^2+y_1^2+z_1^2=am;\quad x_1\equiv\xi_1;\quad y_1\equiv\lambda_1;\quad z_1\equiv\zeta_1 \pmod{k}$$

is resolvable in integers. Moreover, there exist sequences of progressions $\mathfrak{A}_i$ analogous to those in III.

Leningrad University.

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MATHÉMATIQUES

SUR LE THÉORÈME ERGODIQUE

Par HEINRICH HILMY

(Présenté par S. N. Bernstein, de l'Académie, le 20. IV. 1939)

1. Le théorème ergodique démontré par G. D. Birkhoff (1) [voir aussi A. Khintchine (2)] affirme dans sa première partie l'existence, pour press que tous les points de l'espace, d'une certaine valeur limite moyenne par rapport au temps, en supposant qu'il existe une mesure invariante, la mesure de tout l'espace étant finie. La seconde partie du même théorème affirme que dans le cas de l'indécomposabilité métrique de l'espace cette valeur limite est la même pour presque tous les points de l'espace. La seconde partie du théorème ergodique avait été généralisée par W. Stepanoff (3) au cas où la mesure de tout l'espace est infinie [voir aussi E. Hopf (4)].

Dans cette Note nous généralisons, pour le cas d'un espace de mesure invariante infinie, le théorème ergodique fondamental sans supposer l'indécomposabilité métrique (la transitivité forte) du système dynamique.

2. Nous considérons les mouvements des points dans un espace métrique M. Le symbole $f(p, t)$ désigne la position du point $p \subset M$ à un instant du temps t; $f(p, 0) = p$. Supposons $f[f(p, t), \tau] = f(p, t+\tau)$. Nous nommons trajectoire l'ensemble $\{f(p, t)\}$ de tous les points de la forme $f(p, t)$ pour p fixe et pour toute valeur réelle de t, et le point p — point initial de la trajectoire. Soit $A \subset M$ un ensemble arbitraire; le signe $f(A, t)$ désigne l'ensemble de tous les points de la forme $f(p, t)$ où t est fixe et où $p \subset A$. L'ensemble A est dit invariant, si $f(A, t) = A$ pour toute valeur réelle de t.

Admettons, comme on fait habituellement pour les systèmes dynamiques, que les trajectoires dépendent d'une manière continue des conditions initiales.

Supposons enfin qu'il existe dans l'espace M une mesure. Nous disons que la mesure est invariante, si pour tout ensemble mesurable * $Q \subset M$ de mesure finie, la condition $\text{mes}\, f(Q, t) = \text{mes}\, Q$ est satisfaite pour tout t.

3. Soit $Q \subset M$ un ensemble mesurable. Considérons la fonction

$$F(p) = \begin{cases} 1, & \text{si } p \subset Q, \\ 0, & \text{si } p \not\subset Q \end{cases}$$

* Dans la suite nous supposons la mesurabilité B.

et déterminons la fonction $\varphi_Q(p, t)$ comme il suit:

$$\varphi_Q(p, t) = \int_0^t F[f(p, \lambda)]\, d\lambda.$$

Cette intégrale existe pour tout $p \subset M$ et pour toute valeur de t.

La $\lim \frac{1}{t}\varphi_Q(p, t)$ pour $t \to \infty$, si elle existe, sera nommée «la probabilité par rapport au temps» ou simplement «la probabilité» du séjour du point p dans l'ensemble Q. Désignons cette limite par le symbole $P\{f(p, t) \subset Q\}$. Dans le cas où cette limite n'existe pas, nous considérons $\liminf \frac{1}{t}\varphi_Q(p, t)$ et $\limsup \frac{1}{t}\varphi_Q(p, t)$, toutes les deux pour $t \to \infty$, et nous les nommerons respectivement probabilité inférieure et probabilité supérieure du séjour du point p dans l'ensemble Q, en les désignant respectivement par les symboles $P_*\{f(p, t) \subset Q\}$ et $P^*\{f(p, t) \subset Q\}$.

Notons encore que nous ne démontrerons pas la mesurabilité des ensembles, que nous allons employer dans la suite; on rencontre ces ensembles habituellement en étudiant les phénomènes ergodiques et leur mesurabilité est établie pour les conditions imposées au système dynamique.

4. Lemme de Birkhoff-Khintchine. *Soit* Γ *un ensemble invariant possédant une mesure invariante, et* $\Gamma_0 \subset \Gamma$ *un ensemble de mesure finie. Supposons que pour tous les points* $p \subset \Gamma$ *la condition*

$$P^*\{f(p, t) \subset \Gamma_0\} > \beta, \quad [P_*\{f(p, t) \subset \Gamma_0\} < \alpha]$$

soit satisfaite et désignons par Γ_k *l'ensemble de tous les points* $p \subset \Gamma$ *pour lesquels l'inégalité*

$$\frac{1}{l}\varphi_{\Gamma_0}(p, l) > \beta\,(< \alpha)$$

soit vérifiée au moins pour une valeur entière de l *qui satisfait à l'inegalité* $0 < l \leqslant k$. *Si dans ces hypothèses* mes $\Gamma_k < +\infty$ *pour tout nombre entier* k, *nous avons*:

$$\int_{\Gamma_k} \varphi_{\Gamma_0}(p, 1)\, dp > \beta \operatorname{mes} \Gamma_k < (< \alpha \operatorname{mes} \Gamma_k). \tag{1}$$

La démonstration de ce lemme forme une partie importante des raisonnements au moyen desquels on démontre le théorème ergodique pour les espaces de mesure finie. On peut trouver ces raisonnements dans les travaux de Birkhoff [1] et de A. Khintchine [2].

5. Nous dirons que l'ensemble $Q \subset M$ est un ensemble régulier, s'il est mesurable et si pour tout nombre T non-négatif on a

$$0 \leqslant \operatorname{mes} \sum_{|t| \leqslant T} f(Q, t) < +\infty.$$

Théorème ergodique. *Si dans l'espace* M, *dans lequel est déterminé le système dynamique, la mesure est invariante, alors quel que soit l'ensemble régulier* $Q \subset M$, *pour tous les points* $p \subset M$, *sauf peut être pour un ensemble de mesure nulle, la probabilité* $P\{f(p, t) \subset Q\}$ *existe.*

Désignons par W l'ensemble de tous les points $p \subset M$ pour lesquels la probabilité $P\{f(p, t) \subset Q\}$ n'existe pas. Nous allons démontrer le théorème par la réduction à l'absurde; supposons que mes $W > 0$. Désignons par $\Delta_1, \Delta_2, \ldots, \Delta_n, \ldots$ la suite de tous les intervalles de la droite des nombres ayant les extrémités rationelles. Les coordonnées des extré-

mités de l'intervalle Δ_n sont désignées par α_n, β_n ($\alpha_n < \beta_n$). Désignons par W_n l'ensemble de tous les points $p \subset \Gamma$ pour lesquels est vérifiée la condition:

$$P_*\{f(p, t) \subset Q\} < \alpha_n,$$
$$P^*\{f(p, t) \subset Q\} > \beta_n.$$

Alors

$$W = \sum_{n=1}^{\infty} W_n;$$

comme mes $W > 0$, il se trouvera un ν naturel tel que mes $W_\nu > 0$.

L'ensemble W_ν est évidemment un ensemble invariant.

Désignons par Γ l'ensemble défini par l'égalité: $\Gamma = W_\nu$, et soit $\Gamma_0 = \Gamma \cdot Q$. L'ensemble Γ_0 n'est pas évidemment vide et, comme $\Gamma_0 \subset Q \cdot \Gamma_0$, il est un ensemble régulier.

De plus il est évident que pour tout point $p \subset \Gamma_0$ sont vérifiées les conditions:

$$P_*\{f(p, t) \subset Q\} < \alpha,$$
$$P^*\{f(p, t) \subset Q\} > \beta,$$

où pour simplifier on a posé $\alpha = \alpha_\nu$, $\beta = \beta_\nu$.

Désignons par Γ_k l'ensemble de tous les points $p \subset \Gamma$ pour lesquels l'inégalité $\frac{1}{l}\varphi_{\Gamma_0}(p, l) > \beta$ est vérifiée au moins pour un nombre entier l satisfaisant à l'inégalité $0 < l \leqslant k$. Il est évident que

$$\Gamma_k \subset \Gamma_{k+1}, \quad \Gamma = \sum_{k=1}^{\infty} \Gamma_k$$

et qu'il existe un N naturel tel que mes $\Gamma_k > 0$ pour tout $k > N$.

Les deux cas sont possibles:

$$\text{mes}\,\Gamma < +\infty,$$
$$\text{mes}\,\Gamma = +\infty.$$

La mesure de Γ étant $< +\infty$, nous avons, en appliquant le lemme formulé plus haut,

$$\int_{\Gamma_k} \varphi_{\Gamma_0}(p, 1)\, dp > \beta \cdot \text{mes}\,\Gamma_k,$$

ou, à la limite, pour $k \to +\infty$:

$$\int_{\Gamma} \varphi_{\Gamma_0}(p, 1)\, dp > \beta\, \text{mes}\,\Gamma. \tag{2}$$

D'une manière analogue, au moyen du même lemme on peut montrer que

$$\int_{\Gamma} \varphi_{\Gamma_0}(p, 1)\, dp < \alpha \cdot \text{mes}\,\Gamma. \tag{3}$$

Les inégalités (2) et (3) sont contradictoires, donc le cas mes $\Gamma < +\infty$ est impossible.

Examinons le cas où mes $\Gamma = +\infty$. Alors il est évident que

$$\frac{1}{k}\varphi_{\Gamma_0}(p, k) = 0$$

si

$$p \subset \Gamma - \sum_{|t|<k} f(\Gamma_0, t),$$

alors

$$\Gamma_k \subset \sum_{|t|<k} f(\Gamma_0, t),$$

et Γ_0 étant un ensemble régulier,

$$\text{mes}\,\Gamma_k \leqslant \text{mes} \sum_{|t|<k} f(\Gamma_0, t) < +\infty.$$

Vu que $\text{mes}\,\Gamma_k > 0$ pour tout $k > N$ nous pouvons écrire en vertu de (1):

$$\frac{1}{\text{mes}\,\Gamma_k}\int_{\Gamma_k} \varphi_{\Gamma_0}(p, 1)\,dp > \beta \qquad (k > N),$$

d'où

$$\liminf_{\substack{k\to\infty \\ k>N}} \frac{1}{\text{mes}\,\Gamma_k}\int_{\Gamma_k} \varphi_{\Gamma_0}(p, 1)\,dp > \beta > 0. \tag{4}$$

Remarquons enfin que

$$\varphi_{\Gamma_0}(p, 1) = 0,$$

si

$$p \subset \Gamma - \sum_{|t|<1} f(\Gamma_0, t);$$

nous trouvons

$$0 \leqslant \int_{\Gamma_k} \varphi_{\Gamma_0}(p, 1)\,dp \leqslant \int_{\Gamma} \varphi_{\Gamma_0}(p, 1)\,dp \leqslant \text{mes} \sum_{|t|<1} f(\Gamma_0, t).$$

Mais alors

$$0 \leqslant \lim_{\substack{k\to\infty \\ k>N}} \frac{1}{\text{mes}\,\Gamma_k}\int_{\Gamma_k} \varphi_{\Gamma_0}(p, 1)\,dp \leqslant \lim_{\substack{k\to\infty \\ k>N}} \frac{\text{mes}\sum_{|t|<1} f(I_0, t)}{\text{mes}\,\Gamma_k} = 0. \tag{5}$$

Les relations (4) et (5) sont contradictoires; donc le cas $\text{mes}\,\Gamma = +\infty$ est aussi impossible.

Le théorème est démontré.

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MATHÉMATIQUES

SUR LE CHANGEMENT DU TEMPS DANS LES SYSTÈMES DYNAMIQUES POSSÉDANT UNE MESURE INVARIANTE

Par M. BEBUTOFF et W. STEPANOFF

(Présenté par S. N. Bernstein, de l'Académie, le 20. IV. 1939)

1. Nous allons considérer dans un espace métrique R ayant une base dénombrable un système dynamique, c'est-à-dire un groupe à un paramètre $f_0(p, t)$ de transformations de R en lui-même, $p \in R, -\infty < t < \infty$, $f_0(p, t) \in R$, qui satisfait aux conditions suivantes:

$$f_0(p, 0) = p;\ f_0[f_0(p, t_1), t_2] = f_0(p, t_1 + t_2);$$

$f_0(p, t)$ est une fonction continue de l'ensemble de variables (p, t).

Si A est un ensemble quelconque situé dans l'espace R, nous désignerons par $f_0(A, t)$ l'ensemble de tous les points $f_0(p, t)$ tels que $p \in A$. Nous allons nommer «le temps» le paramètre t.

Nous supposerons que dans l'espace R est définie une mesure d'ensembles μ qui satisfait aux axiomes ordinaires de la mesure régulière (extérieure) de Carathéodory et telle que pour tout point $p \in R$ il existe un voisinage $U(p)$ dont la mesure est finie.

En outre nous supposerons que cette mesure est invariante par rapport au groupe $f_0(p, t)$, c'est-à-dire que l'on a $\mu f_0(A, t) = \mu A$. Supposons encore défini dans l'espace R un système dynamique $f_1(p, t')$ tel que pour tout $p \in R$ et tout t il existe une valeur de t' satisfaisant à la relation suivante

$$f_0(p, t) = f_1(p, t') \qquad (1)$$

et tout t' en équation (1) correspond à t.

L'équation (1), à la condition initiale: $t' = 0$ pour $t = 0$, définit pour un point fixe p (si p n'est pas un point de repos) t' comme une fonction continue de t, $t' = t'(p, t)$. Cette fonction est une fonction monotone qui n'est nulle part constante. Inversement, t est une fonction continue et monotone de t', $t = t(p, t')$.

Nous pouvons supposer, en remplaçant, s'il est nécessaire, t' par $-t'$, que ces deux fonctions sont croissantes.

Dans ces conditions on peut introduire dans l'espace R une mesure μ^* qui sera invariante par rapport au systéme $f_1(p, t')$ et telle qu'un ensemble ouvert ayant une mesure μ positive, aura une mesure μ^* positive.

2. Remarquons que si P_0 est l'ensemble des points de repos du système $f_0(p, t)$ et que P_1 est l'ensemble des points de repos du système $f_1(p, t')$,

on a $P_0 = P_1$. Comme pour $A \subset P_0 = P_1$ chaque mesure est invariante, il suffit de démontrer notre assertion pour l'ensemble $M = R - P_0$.

Soit $E \subset M$, alors l'ensemble

$$\Phi(E; -T, T) = \sum_{-T \leqslant t \leqslant T} f_0(E, t)$$

sera appelé le tube fini sur E de longueur $2T_0$ par rapport au temps; un ensemble F fermé dans Φ est nommé une section locale de Φ, si pour tout point $p \in \Phi$ il n'existe qu'un nombre t_p tel que l'on a: $|t_p| \leqslant 2T_0$, $f_0(p, t_p) \in F$.

Pour tout point $p \in M$ il existe deux nombres τ_p et δ_p tels que le tube fini $\Phi(S(p, \delta_p); -(\tau_p, \tau_p)$ a une section locale F_p, et en même temps nous choisissons δ de manière à avoir $\mu\Phi < \infty$*. Pour tout ensemble $Q \subset F_p$ mesurable B on peut définir la mesure

$$\bar{\mu}Q = \frac{1}{\tau}\mu[\Phi(Q; 0, \tau)], \quad 0 < \tau \leqslant \tau_p.$$

On établit que cette définition est indépendante de τ et que pour tout ensemble $A \subset \Phi(F_p; -\tau_p, \tau_p)$, mesurable B, on a

$$\mu A = \int_{F_p} d\bar{\mu} \int_{-\tau_p}^{\tau_p} \chi[f_0(p, t)]\, dt,$$

où $\chi[p]$ est la fonction caractéristique de A.

3. Nous allons construire maintenant la mesure μ^* qui est invariante par rapport au système $f_1(p, t')$.

Pour chaque point p de M nous construisons une section locale F_p du tube fini $\Phi[S(p, \delta_p); -3\tau_p, 3\tau_p]$, section qui contient p, et le tube fini $\Phi(F_p; -\tau_p, \tau_p)$.

Comme $\Phi(F_p; -\tau_p, \tau_p)$ inclut un voisinage du point p, il existe une suite dénombrable $\Phi(F_1; -\tau_1, \tau_1), \ldots, \Phi(F_n; -\tau_n, \tau_n), \ldots$ telle qu'on a

$$\sum_{n=1}^{\infty} \Phi(F_n; -\tau_n, \tau_n) = M.$$

Soit donné un ensemble $A \subset M$ mesurable B. Désignons:

$$A_1 = A \cdot \Phi_1, \quad A_n = \Big(A - \sum_{1}^{n-1} A_k\Big) \cdot \Phi_n \qquad (n = 2, 3, \ldots)$$

où $\Phi_n = \Phi(F_n; -\tau_n, \tau_n)$, et définissons

$$\mu^* A_n = \int_{F_n} d\bar{\mu}_n \int_{t'(p, -\tau_n)}^{t'(p, \tau_n)} \chi_n[f_1(p, t')]\, dt' \text{ et } \mu^* A = \sum_{1}^{\infty} \mu^* A_n,$$

$\chi_n[p]$ étant la fonction caractéristique de A_n, et $\bar{\mu}_n$ étant la mesure $\bar{\mu}$, définie sur la section F_n. On peut démontrer que cette définition est indépendante du choix du système $\{\Phi_n\}$ et que la mesure μ^* est invariante par rapport au système dynamique $f_1(p, t')$.

4. Considérons un cas particulier.

Dans l'espace R, où l'on a défini le système dynamique $f_0(p, t)$ à mesure invariante μ, soit donnée une fonction continue $\lambda(p) > 0$, $p \in R$, telle que pour tout point $p \in R$ les intégrales

$$\int_{-\infty}^{0} \lambda[f_0(p, t)]\, dt \quad \text{et} \quad \int_{0}^{\infty} \lambda[f_0(p, t)]\, dt$$

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* L'existence d'une section locale pour un tube suffisamment petit a été prouvée par le premier des auteurs de la présente Note.

sont divergentes. Définissons une substitution du temps

$$t'(p, t) = \int_0^t \lambda[f_0(p, t)]\, dt \qquad (2)$$

et un nouveau système dynamique $f_1(p, t') = f_0(p, t)$, où t' et t satisfont à la relation (2). Dans ce cas on a

$$\mu^* A_n = \int_{p \in F_n} d\bar{\mu}_n \int_{t'(p,-\tau_n)}^{t'(p,\tau_n)} \chi_n[f_1(p, t')]\, dt' = \int_{F_n} d\bar{\mu}_n \int_{-\tau_n}^{\tau_n} \chi_n[f_0(p, t)]\, \lambda[f_0(p, t)]\, dt =$$

$$= \int_{\Phi(F_n;-\tau_n,\tau_n)} \chi_n[p]\, \lambda(p)\, d\mu = \int_{A_n} \lambda(p)\, d\mu,$$

d'où l'on obtient pour tout ensemble A mesurable B: $\mu^* A = \int_A \lambda(p)\, d\mu$.

Si la substitution du temps (2) a lieu dans un système dynamique défini par les équations différentielles

$$\frac{dx_i}{dt} = X_i(x_1, \ldots, x_n) \quad (i = 1, 2, \ldots, n) \qquad (3)$$

dont les seconds membres, ainsi que $\lambda(x_1, \ldots, x_n)$ admettent les dérivées partielles continues du premier ordre, la relation (2) nous donne:

$$dt' = \lambda(x_1, \ldots, x_n)\, dt,$$

et nous obtenons ce fait connu: si le système (3) possède un invariant intégral

$$\int \ldots \int M dx_1 \ldots dx_n, \qquad (4)$$

$M(x_1, \ldots, x_n) > 0$ admettant les dérivées premières continues, le système

$$\frac{dx_i}{dt} = \frac{X_i}{\lambda} \quad (i = 1, 2, \ldots, n)$$

possède l'invariant intégral $\int \ldots \int M \lambda\, dx_1 \ldots dx_n$.

A l'aide de cette substitution le second des auteurs a obtenu une extension du théorème ergodique pour les systèmes dynamiques indécomposables ayant une mesure invariante, dans le cas où la mesure de l'espace est infinie (1). Pour pouvoir utiliser la mesure variée, l'auteur s'est borné aux systèmes de la forme (3) et à la mesure invariante de la forme (4). D'après les résultats de la Note présente cette généralisation s'étend immédiatement aux systèmes dynamiques arbitraires situés dans un espace métrique ayant une base dénombrable avec une mesure invariante arbitraire satisfaisant aux axiomes de Carathéodory.

Institut Mathématique.
Université de Moscou.

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MATHÉMATIQUES

SUR LES FONCTIONS DE GREEN COMPLÈTEMENT NON-NÉGATIVES DES OPÉRATEURS DIFFÉRENTIELS ORDINAIRES

Par M. KREIN et G. FINKELSTEIN

(Présenté par S. N. Bernstein, de l'Académie, le 28. V. 1939)

1. Soit

$$L(y) = \sum_{k=0}^{m} l_k(x) \frac{d^k y}{dx^k}$$

un opérateur différentiel dont les coefficients $l_k(x)$ $(k = 0,1, \ldots, m)$ sont des fonctions continues dans l'intervalle fermé (a, b) et $l_m(x) \neq 0$ pour $a \leqslant x \leqslant b$.

Soit $G(x, s)$ $(a \leqslant x, s \leqslant b)$ une fonction de Green de l'opérateur $L(y)$. Il est connu, que cette fonction admet toujours la représentation:

$$G(x, s) = \begin{cases} \sum_{j=1}^{p} \psi_j(x)\, \chi_j(s) & (x \leqslant s), \\ \sum_{j=1}^{q} \psi_j^*(x)\, \chi_j^*(s) & (x \geqslant s), \end{cases} \tag{1}$$

où les fonctions $\psi_1, \ldots, \psi_p$ ainsi que les fonctions $\psi_1^*, \ldots, \psi_q^*$ sont des solutions linéairement indépendantes de l'équation homogène: $L(y) = 0$. On peut montrer que les fonctions $\chi_1, \ldots, \chi_p$ de même que les fonctions $\chi_1^*, \ldots \chi_q^*$ sont aussi linéairement indépendantes dans tout sous-intervalle de l'intervalle (a, b).

Il est aisé de voir qu'on a toujours $p + q \geqslant m$. L'égalité $p + q = m$ a lieu dans le cas et dans ce cas seulement, où la fonction de Green $G(x, s)$ correspond à un système de conditions limites formé de p conditions relatives à l'extrémité $x = a$ et q conditions relatives à l'extrémité $x = b$.

Dans le cas, où $G(x, s) \equiv 0$ pour $x \leqslant s$ (où $x \geqslant s$), la fonction de Green $G(x, s)$ correspond aux conditions

$$y(a) = y'(a) = \ldots = y^{(m-1)}(a) = 0,$$

ou aux conditions

$$y(b) = y'(b) = \ldots = y^{(m-1)}(b) = 0$$

respectivement. Dans ce cas nous posons $p = 0$ (resp. $q = 0$) et nous appelons $G(x, s)$ fonction de Cauchy.

2. D'après la terminologie de F. Gantmakher et M. Krein [1] la matrice $A = \| a_{ik} \|_1^n$ est dite complètement non-négative, si tous ses mineurs

$$A\begin{pmatrix} i_1 i_2 \dots i_r \\ k_1 k_2 \dots k_r \end{pmatrix} = \begin{vmatrix} a_{i_1 k_1} & \dots & a_{i_1 k_r} \\ \dots & \dots & \dots \\ a_{i_2 k_1} & \dots & a_{i_2 k_r} \end{vmatrix} \quad \left(1 \leqslant \begin{matrix} i_1 < i_2 < \dots < i_r \\ k_1 < k_2 < \dots < k_r \end{matrix} \leqslant n \right)$$

sont non-negatifs.

Dans ce qui suit nous aurous besoin des deux lemmes suivants concernant ces matrices [voir [1], § 1, la proposition 3°, et § 2, le lemme 2].

Lemme 1. *Si la matrice* $A = \| a_{ik} \|_1^n$ *est complètement non-négative et*

$$A\begin{pmatrix} 1\,2 \dots r \\ 1\,2 \dots r \end{pmatrix} = 0,$$

on a alors

$$A\begin{pmatrix} 1\,2 \dots n \\ 1\,2 \dots n \end{pmatrix} = 0.$$

Lemme 2. *La matrice* $A = \| a_{ik} \|_1^n$ *étant complètement non-négative, si*

$$A\begin{pmatrix} 1\, i_2 \dots i_r\, n \\ 1\, k_2 \dots k_r\, n \end{pmatrix} = 0 \quad \left(1 < \begin{matrix} i_2 < \dots < i_r \\ k_2 < \dots < k_r \end{matrix} < n \right)$$

et si

$$A\begin{pmatrix} 1\, i_2 \dots i_r \\ 1\, k_2 \dots k_r \end{pmatrix} \neq 0, \quad A\begin{pmatrix} i_2 \dots i_r\, n \\ k_2 \dots k_r\, n \end{pmatrix} \neq 0,$$

le rang de la matrice A est égal à r.

3. En accord avec la définition correspondante pour les matrices, une fonction $G(x, s)$ $(a \leqslant x, s \leqslant b)$ est dite complètement non-négative si pour tout $n = 1, 2, \dots$ la condition suivante est remplie:

$$G\begin{pmatrix} x_1 x_2 \dots x_n \\ s_1 s_2 \dots s_n \end{pmatrix} = | G(x_i, s_k) |_1^n \geqslant 0 \text{ pour } a \leqslant \begin{matrix} x_1 < x_2 < \dots < x_n \\ s_1 < s_2 < \dots < s_n \end{matrix} \leqslant b \quad (2)$$

et, par conséquent, la matrice $\| G(x_i, s_k) \|_1^n$ est complètement non-négative pour le choix indiqué de x_i et s_i $(i = 1, 2, \dots n)$.

La fonction $G(x, s)$ est dite oscillatoire, si le signe $=$ est exclu dans (2) pour $x_i = s_i$ $(i = 1, 2, \dots n)$ et si d'ailleurs

$$G(x, s) > 0 \quad \text{pour} \quad a < x, s < b.$$

Les opérateurs $L(y)$ possédant des fonctions de Green oscillatoires ont certaines propriétés remarquables *. A cause de cela le théorème suivant ne manque pas d'intérêt.

Théorème. *Si la fonction de Green ayant la représentation* (1) *est complètement non-négative, l'inégalité*

$$G\begin{pmatrix} x_1 x_2 \dots x_n \\ s_1 s_2 \dots s_n \end{pmatrix} > 0 \left(a < \begin{matrix} x_1 < x_2 < \dots < x_n \\ s_1 < s_2 < \dots < s_n \end{matrix} < b;\ n = 1, 2, \dots \right)$$

a lieu dans le cas et dans ce cas seulement, où les conditions suivantes sont remplies:

$$s_i < x_{i+p} \ (i = 1, 2, \dots n-p), \quad x_i < s_{i+q} \ (i = 1, 2, \dots n-q). \quad (3)$$

En particulier, toute fonction de Green complètement non-négative est oscillatoire, à moins qu'elle ne soit une fonction de Cauchy de l'opérateur $L(y)$.

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* Voir à ce sujet la Note [2] de M. Krein. Dans cette note on étudie les opérateurs, possédant des fonctions de Green oscillatoire symétriques. A l'aide du théorème qui suit, les résultats de cette Note peuvent être étendus au cas non-symétrique. Voir la Note de F. Gantmakher [3] concernant les noyaux de Kellog non-symétriques et la Note de M. Krein qui va paraître dans ces Comptes Rendus (Doklady).

Démonstration. La nécessité de la condition (3) s'obtient presque immédiatement. En effet, si par exemple la première des conditions (3) n'est pas remplie, $s_1 \geqslant x_{p+1}$, on a d'après (1)

$$G(x_i, s_k) = \sum_{j=1}^{p} \psi_j(x_i)\,\chi_j(s_k) \quad \text{pour} \quad i = 1, 2, \ldots p+1, \; k = 1, 2, \ldots n,$$

et, par conséquent, le déterminant (2) dont les $p+1$ premières lignes ne sont pas linéairement indépendantes est nul.

Si, en général, pour un k quelconque $s_k \geqslant x_{k+p}$, on a d'après ce que l'on vient de montrer:

$$G\begin{pmatrix} x_{i_1} x_{i_2} \ldots x_{i_{n-k+1}} \\ s_k \; s_{k+1} \ldots s_n \end{pmatrix} = 0 \quad \text{pour} \quad 1 \leqslant i_1 < i_2 < \ldots < i_{n-k+1} \leqslant n,$$

car ici $s_k > x_{i_{p+1}}$. Donc, le déterminant (2) est encore nul, car ses $n-k+1$ dernières colonnes ne sont pas linéairement indépendantes.

Le cas où quelques-unes des conditions du deuxième groupe de (3) ne sont pas remplies peut être discuté d'une façon analogue.

Pour la démonstration de la suffisance des conditions (3) nous nous bornons au cas le plus difficile, où $G(x, s)$ n'est pas une fonction de Cauchy ($p \geqslant 1$, $q \geqslant 1$). Nous allons poursuivre la démonstration en passant de n à $n+1$. Montrons d'abord que

$$G(x, s) > 0 \quad \text{pour} \quad a < x, s < b. \tag{4}$$

À cet effet admettons le contraire, c'est-à-dire, qu'il existe deux nombres $x_0, s_0 > a$ et $< b$), $G(x_0, s_0) = 0$. On trouve de (2)

$$G\begin{pmatrix} x_0 x \\ s_0 s \end{pmatrix} = -G(x_0, s)\cdot G(x, s_0) \geqslant 0 \quad \text{pour} \quad a < \begin{matrix} x_0 < x \\ s_0 < s \end{matrix} < b.$$

En égard à ce que $G(x, s) \geqslant 0$ $(a \leqslant x, s \leqslant b)$ on en conclut que $G(x_0\, s_0) \equiv 0$ pour $s_0 \leqslant s < b$ ou bien

$$G(x, s_0) \equiv 0 \quad \text{pour} \quad x_0 \geqslant x < b.$$

Supposons, par exemple, la dernière identité vérifiée. En vertu de (1) cette identité n'est possible que dans le cas où $\chi_1^*(s_0) = \chi_2^*(s_0) = \ldots = \chi_q^*(s_0) = 0$, d'où

$$G(x, s_0) = 0 \quad \text{pour} \quad s_0 \leqslant x \leqslant b. \tag{5}$$

Comme la $(n-1)$-ième dérivée de la fonction $G(x, s_0)$ a une discontinuité au point $x = s_0$, il existe un point $x_1 < s_0$ tel que $G(x, s_0) \not\equiv 0$.

En vertu de (5) et de l'inégalité (2) pour $n = 2$ on obtient:

$$G\begin{pmatrix} x_1 x \\ s \; s_0 \end{pmatrix} = -G(x_1, s_0)\cdot G(x, s) \geqslant 0 \quad \text{pour} \quad a < \begin{matrix} s_0 < x \\ s < s_0 \end{matrix} < b.$$

Il en suit que

$$G(x, s) \equiv 0 \quad \text{pour} \quad s_0 < x < b \quad \text{et} \quad a < s < s_0.$$

Or, en vertu de (1) cela n'est possible que dans le cas où $\psi_1^*(x) \equiv \ldots \equiv \equiv \psi_q^*(x) \equiv 0$ pour $s_0 < x < b$, ou bien $\chi_1^*(s) \equiv \ldots \equiv \chi_q^*(s) \equiv 0$ pour $a < s < s_0$. Mais l'un et l'autre cas sont impossibles pour $q \neq 0$. L'inégalité (4) est donc établie.

Admettons maintenant qu'il existe deux systèmes particuliers $x_1^0 < x_2^0 < \ldots < x_n^0$ $(a < x_1^0, x_n^0 < b)$ et $s_1^0 < s_2^0 < \ldots < s_n^0$ $(a < s_1^0, s_n^0 < b)$ liés entre eux par les conditions (3) et tels que

$$G\begin{pmatrix} x_1^0 x_1^0 \ldots x_n^0 \\ s_1^0 \; s_2^0 \ldots s_n^0 \end{pmatrix} = 0.$$

Nos raisonnements étant inductifs, nous pouvons supposer que

$$G\begin{pmatrix} x_1^0 \dots x_{n-1}^0 \\ s_1^0 \dots s_{n-1}^0 \end{pmatrix} > 0 \quad \text{et} \quad G\begin{pmatrix} x_2^0 \dots x_n^0 \\ s_2^0 \dots s_n^0 \end{pmatrix} > 0.$$

Cela posé, on aura d'après le lemme 2 l'identité suivante:

$$G\begin{pmatrix} x_1 \dots x_n \\ s_1 \dots s_n \end{pmatrix} \equiv 0 \quad \text{pour} \quad \begin{matrix} x_1^0 < x_1 < \dots < x_n < x_n^0 \\ s_1^0 < s_1 < \dots < s_n < s_n^0 \end{matrix}. \tag{6}$$

Montrons que l'intervalle (s_1^0, s_n^0) n'a pas de points intérieurs communs avec l'intervalle (x_1^0, x_n^0). En effet, en admettant le contraire on pourrait prendre à l'intérieur de ces deux intervalles un système de points communs $c_1 < c_2 < \dots < c_n$, pour lesquels on aurait en vertu de (6) l'identité:

$$G\begin{pmatrix} c_1 \dots c_{n-1} x \\ c_1 \dots c_{n-1} c_n \end{pmatrix} \equiv 0 \quad \text{pour} \quad x_1^0 < x < x_n^0.$$

En développant le déterminant d'après les éléments de la dernière ligne, on met l'identité sous la forme

$$\mu_1 G(x, c_1) + \mu_2 G(x, c_2) + \dots + \mu_n G(x, c_n) \equiv 0 \quad \text{pour} \quad x_1^0 < x < x_n^0.$$

Ici $\mu_n \neq 0$ d'après la supposition de l'induction. Mais une telle identité est impossible, car la $(n-1)$-ième dérivée de la fonction $G(x, c_i)$ a la seule discontinuité au point $x = c_i$ $(i = 1, 2, \dots n)$.

Ainsi les intervalles (x_1^0, x_n^0) et (s_1^0, s_n^0) n'ont pas de points communs intérieurs. Soit par exemple $x_n^0 \leqslant x_1^0$. En vertu de la condition (3) cela entraîne l'inégalité $n \leqslant p$. D'autre part, si $n \leqslant p$, on déduit de l'identité (6) et du lemme 2 que

$$G\begin{pmatrix} x_1 \dots x_p \\ s_1 \dots s_p \end{pmatrix} \equiv 0 \quad \text{pour} \quad \begin{matrix} x_1^0 < x_1 < \dots < x_p < x_n^0 \\ s_1^0 < s_1 < \dots < s_p < s_n^0 \end{matrix}.$$

En outre, ayant $x_n^0 \geqslant s_1^0$ on déduit de (1) que pour les valeurs considérées de x_i et s_i $(i = 1, 2, \dots p)$ on a aussi:

$$G\begin{pmatrix} x_1 \dots x_p \\ s_1 \dots s_p \end{pmatrix} = |\psi_i(x_k)|_1^p \cdot |\chi_i(s_k)|_1^p.$$

Par conséquent, on a

$$|\psi_i(x_k)|_1^p \equiv 0 \quad \text{pour} \quad x_1^0 < x_1 < \dots < x_p < x_n^0, \tag{7}$$

ou bien

$$|\chi_i(s_k)|_1^p \equiv 0 \quad \text{pour} \quad s_1^0 < s_1 < \dots < s_p < s_n^0. \tag{8}$$

Or, (7) etraîne une relation linéaire entre les fonctions $\psi_1, \dots, \psi_n$ dans l'intervalle (x_1^0, x_n^0) et (8) — une relation linéaire des fonctions $\chi_1, \dots, \chi_n$ dans l'intervalle (s_1^0, s_n^0). Mais l'un et l'autre cas sont impossibles.

On discute le cas, où $s_n^0 \leqslant x_1^0$, d'une façon tout-à-fait analogue.

Le théorème est donc démontré.

Université d'État.
Odessa.

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MATHÉMATIQUES

SUR UN PROBLÈME-MINIMUM

Par J. GERONIMUS

(Présenté par S. N. Bernstein, de l'Académie, le 28, V. 1939)

La solution du problème-minimum dont il s'agit est donnée par le Théorème. *Pour chaque polynôme trigonométrique d'ordre n*

$$G(\theta) = R \sum_{k=0}^{n} \gamma_k e^{i(n-k)\theta}, \qquad \gamma_k = \alpha_k + i\beta_k \tag{1}$$

satisfaisant à la condition

$$\alpha_0\lambda_0 + \beta_0\mu_0 = 1, \tag{2}$$

l'inégalité suivante a lieu

$$\int_0^{2\pi} \left| \frac{G(\theta)}{q(z)} \right| d\theta \geqslant 4, \qquad z = e^{i\theta} \tag{3}$$

où

$$q(z) = \sum_{k=0}^{s} \sigma_k z^{s-k}, \qquad \frac{1}{\sigma_0} = \lambda_0 + i\mu_0, \tag{4}$$

*est un polynôme donné de degré $s \leqslant 2n-1$ dont toutes les racines se trouvent dans le domaine fermé $|z| \leqslant 1$; l'égalité n'a lieu que pour le polynôme**

$$G^*(\theta) = R\{q(z)\, z^{n-s}\}, \qquad z = e^{i\theta}. \tag{5}$$

Ce résultat n'est pas nouveau en principe après les recherches faites par S. Bernstein sur les polynômes rationnels ([2], [3]) — cependant il nous semble que la méthode que nous avons employée pour prouver ce théorème peut être utilisée pour la solution de problèmes analogues.

Pour démontrer le théorème nous trouverons les premiers membres du développement de sgn $G^*(\theta)$ en série de Fourier; nous avons:

$$\operatorname{sgn} G^*(\theta) = \operatorname{sgn} R\left\{ \frac{q(z)}{|q(z)|}\, z^{n-s} \right\} = \operatorname{sgn} \cos n\varphi, \qquad z = e^{i\theta}; \tag{6}$$

où nous avons posé:

$$e^{in\varphi} = \frac{q(z)}{|q(z)|}\, z^{n-s}, \qquad z = e^{i\theta}. \tag{7}$$

* Dans le cas particulier où $q(z)$ est le carré d'un polynôme le problème a été résolu dans notre Note([1]).

Cela étant, nous trouvons le développement cherché

$$\operatorname{sgn} G^*(\theta) = \operatorname{sgn}\cos n\varphi = \frac{4}{\pi} R \sum_{k=0}^{\infty} \frac{(-1)^k e^{in\varphi(2k+1)}}{2k+1} =$$

$$= \frac{4}{\pi} \sum_{k=0}^{\infty} \frac{(-1)^k}{2k+1} \left\{ \frac{q(z)}{|q(z)|} z^{n-s} \right\}^{2k+1}, \qquad z = e^{i\theta}, \tag{8}$$

d'où nous obtenons aisément:

$$\frac{\operatorname{sgn} G^*(\theta)}{|q(z)|} = \frac{4}{\pi} R \left\{ \frac{z^n}{z^s \overline{q}\left(\frac{1}{z}\right)} \right\} + R \sum_{k=3n-s}^{\infty} A_k z^k =$$

$$= \frac{4}{\pi} R \left\{ \frac{z^n}{\sigma_0} \right\} + R \sum_{k=n+1}^{\infty} B_k z^k, \qquad z = e^{i\theta}. \tag{9}$$

En multipliant les deux parties par un polynôme arbitraire $G(\theta)$ d'ordre n et en intégrant nous trouvons l'inégalité cherchée

$$\left| \int_0^{2\pi} \frac{\operatorname{sgn} G^*(\theta)\, G(\theta)\, d\theta}{|q(z)|} \right| = \frac{4}{\pi} \left| \int_0^{2\pi} R \left\{ \frac{z^n}{\sigma_0} \right\} G(\theta)\, d\theta \right| =$$

$$= 4 |\alpha_0 \lambda_0 + \beta_0 \mu_0| = 4 \leqslant \int_0^{2\pi} \left| \frac{G(\theta)}{q(z)} \right| d\theta, \tag{10}$$

l'égalité n'ayant lieu que pour le polynôme $G(\theta) \equiv G^*(\theta)$.

De ce théorème on obtient aisément comme cas particuliers les inégalités suivantes:

$$\int_{-1}^{1} \frac{|b_0 x^n + b_1 x^{n-1} + \ldots + b^n|}{\sqrt{(x+a_1)(x+a_2)\ldots(x+a_s)}}\, dx \geqslant \frac{|b_0|}{2^{n-1}} \prod_{k=1}^{s} |\sqrt{a_k+1} - \sqrt{a_k-1}|; \tag{11}$$

$$\int_{-1}^{1} \frac{|b_0 x^n + b_1 x^{n-1} + \ldots + b_n|}{\sqrt{(x+a_1)(x+a_2)\ldots(x+a_s)}} \cdot \frac{dx}{\sqrt{1-x^2}} \geqslant$$

$$\geqslant \frac{|b_0|}{2^{n-2}} \prod_{k=1}^{s} |\sqrt{a_k+1} - \sqrt{a_k-1}|, \tag{12}$$

$\prod_{k=1}^{s} (x+a_k)$ étant un polynôme donné à coefficients réels, positif sur le segment $(-1, +1)$; l'égalité dans (11) n'a lieu que pour le polynôme

$$P^*(x) = \sum_{k=0}^{s} \sigma_k U_{n-k}(x), \quad U_k(x) = \frac{\sin(k+1)\varphi}{\sin\varphi}, \quad (k = 0, 1, \ldots), \; x = \cos\varphi, \tag{13}$$

et dans (12)—pour le polynôme

$$P^{**}(x) = \sum_{k=0}^{s} \sigma_k T_{n-k}(x), \quad T_k(x) = \cos k\varphi, \quad (k = 0, 1 \ldots), \quad x = \cos\varphi; \tag{14}$$

les nombres σ_k sont les coefficients du polynôme

$$\sum_{k=0}^{s} \sigma_k z^{s-k} = \prod_{k=1}^{s} (z+\lambda_k), \quad \lambda_k = a_k - \sqrt{a_k^2-1}, \ |\lambda_k| < 1, \ (k=1, 2, \ldots s). \quad (15)$$

L'inégalité (12) suit du résultat (3) de S. Bernstein *; l'inégalité (11) dans le cas particulier $s=1$ a été trouvée pour la première fois par W. Břečka.

Institut de Mathématiques et de Mécanique.
Université de Kharkoff.

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* S. Bernstein fait une restriction—il suppose que s est pair; de nos considérations il suit que cette restriction peut être rejetée.

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THEORY OF ELASTICITY

ON THE SAINT-VENANT'S PROBLEM FOR NATURALLY TWISTED BARS

By A. LOURIE and G. JANELIDZE

(Communicated by N. I. Muskhelishvili, Member of the Academy, 5. V. 1939)

Flexure by a Couple. We have*:

$$\left.\begin{aligned} &\sigma_0^{33} = -\frac{M}{I_2}\,x_1,\quad \sigma_0^{11}=\sigma_0^{12}=\sigma_0^{13}=\sigma_0^{23}=0,\\ &u_0^1=\frac{1}{4}\,\frac{\lambda}{\mu\,(3\lambda+2\mu)}\,\frac{M}{I_2}\,(x_1^2-x_2^2)+\frac{1}{2}\,\frac{\lambda+\mu}{\mu\,(3\lambda+2\mu)}\,\frac{M}{I_2}\,x_3^2,\\ &u_0^2=\frac{\lambda}{2\mu\,(3\lambda+2\mu)}\,x_1x_2,\quad u_0^3=-\frac{\lambda+\mu}{\mu\,(3\lambda+2\mu)}\,x_1x_3. \end{aligned}\right\} \qquad (1)$$

In the first approximation the equilibrium equations in the interior and on the lateral surface have the usual form of corresponding equations in Cartesian co-ordinates. The equations (17) of the first communication take in the present case the following form:

$$\left.\begin{aligned} &\sigma_1^{11}=\lambda\vartheta_1+2\mu\,\frac{\partial u_1^1}{\partial x_1}+\frac{2\,(\lambda+\mu)}{3\lambda+2\mu}\,\frac{M}{J_2}\,x_2x_3,\\ &\sigma_1^{22}=\lambda\vartheta_1+\mu\,\frac{\partial u_1^2}{\partial x_2},\\ &\sigma_1^{33}=\lambda\vartheta_1+2\mu\,\frac{\partial u_1^3}{\partial x_3}-\frac{2\,(\lambda+\mu)}{3\lambda+2\mu}\,\frac{M}{J_2}\,x_2x_3,\\ &\sigma_1^{12}=\mu\left(\frac{\partial u_1^1}{\partial x_2}+\frac{\partial u_1^2}{\partial x_1}\right)-\frac{\lambda+\mu}{3\lambda+2\mu}\,\frac{M}{J_2}\,x_1x_3,\\ &\sigma_1^{13}=\mu\left(\frac{\partial u_1^1}{\partial x_3}+\frac{\partial u_1^3}{\partial x_1}\right)-\frac{2\,(\lambda+\mu)}{3\lambda+2\mu}\,\frac{M}{J_2}\,x_1x_2,\\ &\sigma_1^{23}=\mu\left(\frac{\partial u_1^2}{\partial x_3}+\frac{\partial u_1^3}{\partial x_2}\right)+\frac{7\lambda+4\mu}{4\,(3\lambda+2\mu)}\,\frac{M}{J_2}\,x_1^2+\\ &+\frac{\lambda}{4\,(3\lambda+2\mu)}\,\frac{M}{J_2}\,x_2^2+\frac{\lambda+\mu}{2\,(3\lambda+2\mu)}\,\frac{M}{J_2}\,x_3^2. \end{aligned}\right\} \qquad (2)$$

The integrability conditions of the system (2) have in the present case the form:

$$\left.\begin{aligned} &\frac{2\,(\lambda+\mu)}{3\lambda+2\mu}\,\frac{\partial^2 S_1}{\partial x_1^2}+\Delta\sigma_1^{11}=0,\quad \frac{2\,(\lambda+\mu)}{3\lambda+2\mu}\,\frac{\partial^2 S_1}{\partial x_2^2}+\Delta\sigma_1^{22}=0,\\ &\frac{2\,(\lambda+\mu)}{3\lambda+2\mu}\,\frac{\partial^2 S_1}{\partial x_3^2}+\Delta\sigma_1^{33}=0,\\ &\frac{2\,(\lambda+\mu)}{3\lambda+2\mu}\,\frac{\partial^2 S_1}{\partial x_1\partial x_2}+\Delta\sigma_1^{12}=0;\quad \frac{2\,(\lambda+\mu)}{3\lambda+2\mu}\,\frac{\partial^2 S_1}{\partial x_1\partial x_3}+\Delta\sigma_1^{13}=0,\\ &\frac{2\,(\lambda+\mu)}{3\lambda+2\mu}\,\frac{\partial^2 S_1}{\partial x_2\partial x_3}+\Delta\sigma_1^{23}=\frac{M}{J_2}\,\frac{5\lambda+3\mu}{3\lambda+2\mu},\\ &S_1=\sigma_1^{11}+\sigma_1^{22}+\sigma_1^{33},\quad \Delta=\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial x_3^2}. \end{aligned}\right\} \qquad (3)$$

* C. R. Acad. Sci. URSS, XXIV, No. 2 (1939).

The stresses in question we represent in the form:

$$\sigma_1^{ik} = {}^1\sigma_1^{ik} + {}^2\sigma_1^{ik},$$

where ${}^2\sigma_1^{11} = {}^2\sigma_1^{22} = {}^2\sigma_1^{12} = 0$ and ${}^2\sigma_1^{13}$ and ${}^2\sigma_1^{23}$ do not depend on x_3. For the stresses ${}^2\sigma_1^{ik}$ the first four equations (3) are identically satisfied, and the remaining yield:

$$\Delta({}^2\sigma_1^{13}) = 0, \quad \Delta({}^2\sigma_1^{23}) = \frac{M}{J_2}\frac{5\lambda+3\mu}{3\lambda+2\mu}. \tag{4}$$

All equilibrium equations are identically satisfied for ${}^2\sigma_1^{ik}$ with the exception of

$$\frac{\partial({}^2\sigma_1^{13})}{\partial x_1} + \frac{\partial({}^2\sigma_1^{23})}{\partial x_2} = 0, \quad {}^2\sigma_1^{13}\nu_1 + {}^2\sigma_1^{23}\nu_2 = 0. \tag{5}$$

The equations (5) may be satisfied by putting

$${}^2\sigma_1^{13} = \frac{M}{J_2}\frac{5\lambda+3\mu}{3\lambda+2\mu}\frac{\partial\psi}{\partial x_2}; \quad {}^2\sigma_1^{23} = \frac{M}{J_2}\frac{5\lambda+3\mu}{3\lambda+2\mu}\left(-\frac{\partial\psi}{\partial x_1} + \frac{1}{2}x_1^2\right). \tag{6}$$

From (4) and (5) it follows that ψ is a harmonic function satisfying on the contour the condition

$$\psi = \frac{1}{6}x_1^3. \tag{7}$$

For instance, in the case of an ellipse with the half-axes a and b

$$\psi = \frac{a^2}{6(a^2+3b^2)}(x_1^3 - 3x_1x_2^2 + 3b^2x_1).$$

The system of stresses ${}^1\sigma_1^{ik}$ satisfies the equations formally identical with the usual equations of the theory of elasticity in the Cartesian system of co-ordinates, when mass and surface forces are absent.

The end conditions for this system of stresses have, as computations show, the following form:

$$\iint {}^1\sigma_1^{31}do = 0; \quad \iint {}^1\sigma_1^{32}do = M; \quad \iint {}^1\sigma_1^{33}do = 0;$$

$$\iint x_1\,{}^1\sigma_1^{33}do = 0; \quad \iint x_2\,{}^1\sigma_1^{33}do = 0,$$

$$\iint (x_1\,{}^1\sigma_1^{32} - x_2\,{}^1\sigma_1^{31})do = \frac{M}{J_2}B,$$

where

$$B = \iint (x_1^2 + x_2^2)\,x_1do + \frac{5\lambda+3\mu}{3\lambda+2\mu}\iint\left(x_1\frac{\partial\psi}{\partial x_1} + x_2\frac{\partial\psi}{\partial x_2} - \frac{1}{2}x_1^3\right)do.$$

These conditions show that the determination of the system of stresses ${}^1\sigma_1^{ik}$ is formally equivalent to the problem of Saint-Venant on the flexure by a force M applied in the cross-section $x_3 = l$ in the direction of the axis x_2 and the torsion by a couple $\frac{M}{J_2}B$. The solution of this problem is, however, well known (1).

Industrial Institute.
Leningrad.

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THEORY OF ELASTICITY

DEFORMATIONS OF BARS WITH SLIGHTLY CURVED AXES *

By P. RIZ

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3. Torsion. We consider a bar, whose lateral surface is given by the equation

$$f\left(x+\frac{\beta}{2}z^2,\ y\right)=0, \tag{1}$$

or, if we introduce the variables

$$\xi=x+\frac{\beta}{2}z^2,\quad \eta=y,\quad \zeta=z, \tag{2}$$
$$f(\xi,\eta)=0.$$

We solve the torsion problem with the precision up to β^2. The displacements we assume to be of the form:

$$\left.\begin{aligned} u&=-\tau\eta\zeta+\tau\beta u^{(1)}\\ v&=\tau\xi\zeta+\tau\beta v^{(1)}\\ w&=\tau\varphi(\xi,\eta)+\tau\beta w^{(1)}\end{aligned}\right\} \tag{3}$$

where $\varphi(\xi,\eta)$ is the torsion function for the contour $f(\xi,\eta)=0$, $\tau=\frac{M}{\mu T}$ (M is the moment of the twisting couple, μ — the modulus and T—the geometrical torsion stiffness of the prismatical bar).

For the stresses we find:

$$\left.\begin{aligned} &\sigma_{xx}=\lambda\tau\beta\zeta\varphi'_\xi+\tau\beta\sigma^{(1)}_{xx},\quad \sigma_{yy}=\lambda\tau\beta\zeta\varphi'_\xi+\tau\beta\sigma^{(1)}_{yy},\\ &\sigma_{zz}=(\lambda+2\mu)\,\tau\beta\zeta\varphi'_\xi+\tau\beta\sigma^{(1)}_{zz}\quad \sigma_{xy}=\tau\beta\sigma^{(1)}_{xy}\\ &\sigma_{xz}=\mu\tau\,(\varphi'_\xi-\eta)+\tau\beta\sigma^{(1)}_{xz},\\ &\sigma_{yz}=\mu\tau\,(\varphi'_\eta+\xi)+\tau\beta\sigma^{(1)}_{yz}.\end{aligned}\right\} \tag{4}$$

The equilibrium equations are:

$$\left.\begin{aligned} &L^{(1)}_1+(\lambda+\mu)\,\varphi''_{\xi\xi}\zeta=0,\quad L^{(1)}_2+(\lambda+\mu)\,\varphi''_{\xi\eta}\zeta+3\mu\zeta=0,\\ &L^{(1)}_3+(\lambda+2\mu)\,\varphi'_\xi=0.\end{aligned}\right\} \tag{5}$$

The conditions on the lateral surface are:

$$\left.\begin{aligned} M^{(1)}_1+\lambda\zeta\varphi'_\xi f'_\xi+\mu\zeta\,(\varphi'_\xi-\eta)\,f'_\xi&=0,\\ M^{(1)}_2+\lambda\zeta\varphi'_\xi f'_\eta+\mu\zeta\,(\varphi'_\eta+\xi)\,f'_\eta&=0,\\ M^{(1)}_3&=0.\end{aligned}\right\} \tag{6}$$

* For the first part of this paper see C. R. Acad. Sci. URSS, XXIV, № 2 (1939).

The compatibility conditions are:

$$\left.\begin{aligned} N_{11}^{(1)} &= -2(\lambda+\mu)\zeta\varphi'''_{\xi\xi\xi}, & N_{12}^{(1)} &= -2(\lambda+\mu)\zeta\varphi'''_{\xi\xi\eta} \\ N_{22}^{(1)} &= -2(\lambda+\mu)\zeta\varphi'''_{\xi\eta\eta}, & N_{13}^{(1)} &= -(2\lambda+3\mu)\varphi''_{\xi\xi} \\ N_{33}^{(1)} &= 0, & N_{23}^{(1)} &= -(2\lambda+3\mu)\varphi''_{\xi\eta}-3\mu. \end{aligned}\right\} \tag{7}$$

Along with these must be satisfied the conditions in the terminal cross-section expressing the equivalence of the stresses to the twisting couple with the moment M. We find first a particular solution satisfying all conditions except those in the terminal cross-section:

$$\left.\begin{aligned} \sigma_{xx}^{(1)} &= -(\lambda+2\mu)\varphi'_{\xi}\zeta+2\mu\eta\zeta+\zeta\frac{\partial^2 F}{\partial\eta^2}, \\ \sigma_{yy}^{(1)} &= -\lambda\varphi'_{\xi}\zeta+\mu\eta\zeta+\zeta\frac{\partial^2 F}{\partial\xi^2}, \\ \sigma_{zz}^{(1)} &= \nu(\sigma_{xx}^{(1)}+\sigma_{yy}^{(1)}), \\ \sigma_{xz}^{(1)} &= \sigma_{xz}^{(1)}(\xi,\eta), \\ \sigma_{yz}^{(1)} &= \sigma_{yz}^{(1)}(\xi,\eta), \\ \sigma_{xy}^{(1)} &= -\zeta\frac{\partial^2 F}{\partial\xi\partial\eta}-\mu\varphi'_{\eta}\zeta-\mu\xi\zeta. \end{aligned}\right\} \tag{8}$$

Herein $F(\xi,\eta)$ is a biharmonic function satisfying the contour conditions:

$$\left.\begin{aligned} \frac{\partial F}{\partial\eta} &= 0, \\ \frac{\partial F}{\partial\xi}+\mu\xi\eta &= 0; \end{aligned}\right\} \tag{9}$$

$\sigma_{xz}^{(1)}$ and $\sigma_{yz}^{(1)}$ are defined by the conditions:

$$\left.\begin{aligned} \nabla^2\sigma_{xz}^{(1)}+\frac{\partial}{\partial\xi}\nabla^2 F+\mu\varphi''_{\xi\xi} &= 0, \\ \nabla^2\sigma_{yz}^{(1)}+\frac{\partial}{\partial\eta}\nabla^2 F+\mu\varphi''_{\eta\xi}+6\mu &= 0 \end{aligned}\right\} \tag{10}$$

and

$$\sigma_{xz}^{(1)}f'_{\xi}+\sigma_{yz}^{(1)}f'_{\eta}=0. \tag{11}$$

Observe the following relations:

$$\left.\begin{aligned} \iint\sigma_{yz}\,dxdy &= \iint\{\nu\nabla^2 F\cdot\eta-2(\lambda+\mu)\nu\eta\cdot\varphi'_{\xi}+3\mu\nu\eta^2\}\,d\xi d\eta = P_y, \\ \iint\sigma_{xz}\,dxdy &= \iint\{\nu\nabla^2 F\cdot\xi-2(\lambda+\mu)\nu\xi\cdot\varphi'_{\xi}+3\mu\nu\xi\eta\}\,d\xi d\eta = P_x, \end{aligned}\right\} \tag{12}$$

$$\iint\sigma_{zz}\,dxdy=\iint x\sigma_{zz}\,dxdy=\iint y\sigma_{zz}\,dxdy=0. \tag{13}$$

The equations (13) hold only in the cross-section $z=0$.

We add now to the obtained stresses a system of stresses $\sigma_{xz}^{(2)}$, $\sigma_{yz}^{(2)}$ and $\sigma_{zz}^{(2)}$, satisfying the equations of equilibrium and compatibility, leaving the lateral surface free and, at the same time, neutralizing the excessive stresses in the terminal cross-section.

To this end we put

$$\left.\begin{aligned}\sigma_{xz}^{(2)} &= \mu\left(\frac{\partial\psi_0}{\partial\xi}+\frac{\nu P_x}{EJ_\eta}\eta^2\right)+\mu\frac{\partial\bar{\psi}_0}{\partial\xi}+k(\varphi_\xi'-\eta),\\ \sigma_{yz}^{(2)} &= \mu\frac{\partial\psi_0}{\partial\eta}+\mu\left(\frac{\partial\bar{\psi}_0}{\partial\eta}+\frac{\nu P_y}{EJ_\xi}\xi^2\right)+k(\psi_\eta'+\xi),\\ \sigma_{zz}^{(2)} &= -\frac{P_y}{J_\xi}\eta\zeta-\frac{P_x}{J_\eta}\xi\zeta,\end{aligned}\right\} \tag{14}$$

where ψ_0 is the flexure function for the contour $f(\xi, \eta)=0$ satisfying the equation:

$$\nabla^2\psi_0+\frac{2(1+\nu)}{EJ_\xi}P_\eta\cdot\eta=0, \tag{15}$$

and the contour condition

$$\frac{\partial\psi_0}{\partial\xi}f_\xi'+\frac{\partial\psi_0}{\partial\eta}f_\eta'+\frac{\nu P_\eta}{EJ_\xi}\cdot\xi^2 f_\eta'=0. \tag{16}$$

The function $\bar{\psi}_0$ satisfies the conditions:

$$\nabla^2\bar{\psi}_0+\frac{2(1+\nu)\cdot P_\xi}{EJ_\eta}\cdot\xi=0 \tag{17}$$

and

$$\frac{\partial\bar{\psi}_0}{\partial\xi}f_\xi'+\frac{\partial\bar{\psi}_0}{\partial\eta}f_\eta'+\frac{\nu P_\xi}{EJ_\eta}\cdot\eta^2 f_\xi'=0. \tag{18}$$

The constant k may be determined from the equation:

$$\iint(y\sigma_{xz}-x\sigma_{yz})\,dxdy=M. \tag{19}$$

As an example we state the results in the case of a bar with an elliptical cross-section:

$$F=\left(\eta-\frac{\xi^2\eta}{a^2}-\frac{\eta^3}{3b^2}\right)\frac{\mu a^2}{2},$$

$$\sigma_{xz}^{(1)}=\frac{\partial\psi}{\partial\xi},$$

$$\sigma_{yz}^{(1)}=\frac{\partial\psi}{\partial\eta}+\frac{m}{2}\xi^2,$$

where

$$m=-\mu\left[5-2\nu+2\frac{b^2-a^2}{b^2+a^2}\cdot\frac{1-\nu}{1-2\nu}-\frac{a^2}{b^2}(1-2\nu)\right],$$

$$\psi=-\varkappa_1\left\{-\frac{a^2[2(1+\varkappa_2)a^2+b^2]}{3a^2+b^2}\eta+\frac{1}{3}\frac{2a^2+b^2+\frac{1}{2}\varkappa_2(a^2-b^2)}{3a^2+b^2}(\eta^3-3\eta\xi^2)+\right.$$
$$\left.+\frac{1}{6}\varkappa_2\eta^3+\left(1+\frac{\varkappa_2}{2}\right)\eta\xi^2\right\};$$

herein

$$\varkappa_1=\mu\nu\left(1-\frac{b^2-a^2}{b^2+a^2}\cdot\frac{1}{1-2\nu}-\frac{a^2}{b^2}\right)-\frac{m}{2},$$

$$\varkappa_2=\frac{m}{2\mu\nu\left(1-\frac{b^2-a^2}{b^2+a^2}\frac{1}{1-2\nu}-\frac{a^2}{b^2}\right)-m},$$

$$P_x=0,$$

$$P_y=\left(1-\frac{b^2-a^2}{b^2+a^2}\cdot\frac{1}{1-2\nu}-\frac{a^2}{b^2}\right)2\mu\nu J_\xi,$$

$$k=0,\quad \bar{\psi}_0=0.$$

It is of interest to note that in the case of a thin ellipse ($a \gg b$) the stresses due to the original bend may be quite considerable in spite of the smallness of the factor $\tau\beta$. The additional displacements corresponding to the system of stresses $\sigma_{xz}^{(1)}$, etc. have a rather complicated character. We shall determine them only in the case of an elliptical cross-section. In this case

$$u^{(1)} = c_1\xi\eta\zeta + \overline{u}(\xi, \eta),$$
$$v^{(1)} = c_2\eta^2\zeta + \overline{v}(\xi, \eta),$$
$$w^{(1)} = \frac{1}{\mu}\psi(\xi, \eta) + c_4\eta^3 + c_5\xi^2\eta$$

(the values of the constants c_i we do not state).

The displacements corresponding to the system $\sigma_{xz}^{(2)}$, $\sigma_{yz}^{(2)}$ and $\sigma_{zz}^{(2)}$ have the character of displacements caused by flexure and may be easily determined in the general case. In the case of the bar with an elliptical cross-section the torsion causes a flexure in the plane perpendicular to that of the axis of the bar.

4. Extension by a Force Applied in a Cross-Section. The displacements we assume to be

$$\left.\begin{aligned} u &= -\frac{\nu p}{E}\xi + p\beta u^{(1)}, \\ v &= -\frac{\nu p}{E}\eta + p\beta v^{(1)}, \\ w &= -\frac{\nu p}{E}\zeta + p\beta w^{(1)}; \end{aligned}\right\} \tag{20}$$

hence

$$\left.\begin{aligned} &\sigma_{xx} = p\beta\sigma_{xx}^{(1)}; \quad \sigma_{yy} = p\beta\sigma_{yy}^{(1)}; \quad \sigma_{zz} = p + p\beta\sigma_{zz}^{(1)}; \\ &\sigma_{xy} = p\beta\sigma_{xy}^{(1)}; \quad \sigma_{xz} = p\beta\sigma_{xz}^{(1)} - \beta p\mu\frac{\nu}{E}\zeta; \quad \sigma_{yz} = p\beta\sigma_{yz}^{(1)}. \end{aligned}\right\} \tag{21}$$

The equilibrium equations are:

$$L_1^{(1)} = \frac{\mu\nu}{E}; \quad L_2^{(1)} = 0; \quad L_3^{(1)} = 0. \tag{22}$$

The conditions on the lateral surface are:

$$M_1^{(1)} = 0; \quad M_2^{(1)} = 0; \quad M_3^{(1)} + \left(1 - \frac{\mu\nu}{E}\right)\zeta f_\xi' = 0. \tag{23}$$

By means of the substitution $\sigma_{xz}^{(1)} = '\left(\frac{\mu\nu}{E} - 1\right)\zeta + \overline{\sigma}_{xz}$ this problem may be easily reduced to the problem of flexure under the action of the force of weight with the equations:

$$\overline{L}_1 = 1; \quad \overline{L}_2 = 0; \quad \overline{L}_3 = 0; \quad \overline{M}_i = 0. \tag{24}$$

The method of solution of this problem is exposed in Love's book [1] and we shall not state it here. From the formulation of the problem it is obvious that the additional displacements are reduced to the unbending of the bar by the extending force. The results may be easily generalized to the case of a bar, whose axis is not a plane curve and the equation of whose lateral surface has the form

$$f\left(x + \frac{\beta_1 z^2}{2}, \quad y + \frac{\beta_2 z^2}{2}\right) = 0.$$

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PHYSICS

SOME CONTRIBUTIONS TO THE QUANTUM FIELD THEORY

By M. MARKOV

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Quantum electrodynamics involve, as is well known, at the present stage of their development, certain grave difficulties: the point-electron, divergent expression in the highest approximations of the theory, etc.

The difficulties here referred to may at the present time be considered as difficulties characteristic of a theory of any familiar field such as the field of Maxwell, that of Fermi, that of Yukawa, the ψ-field, etc. Accordingly, the solution of these difficulties ought to be a single one.

Upon quantization of field, magnitude F characterizing the given field becomes expanded into a Fourrier series:

$$F=\sum_s \alpha_s (N_s^+ \cdot e^{-i\bar{k}_s\bar{r}} + N_s^- \cdot e^{+i\bar{k}_s\bar{r}}), \tag{1}$$

N_s^+ and N_s^- are considered as operators:

$$[N_s^+ N_\rho^-]_\pm = \delta_{s\rho}. \tag{2}$$

These operators are frequently written out in the following form:

$$N_s^+ = \sqrt{n_s}\, e^{-i\Phi_s}; \quad N_s^- = e^{+i\Phi_s}\sqrt{n_s}, \tag{3}$$

where n_s is a variable of the number of particles; Φ_s is phase.

In contradistinction to ordinary theory we shall next require that the wave phase and the radius vector should be non-commuting operators:

$$\Phi_s X_\mu - X_\mu \Phi_s = 2\pi r_{s\mu} \quad (\mu = 1, 2, 3, 4). \tag{4}$$

The phase is non-dimensional, wherefore $r_{s\mu}$ represents a certain four-dimensional vector of length dimension.

This vector, as will be shown in the subsequent, has in the theory propounded by us the same fundamental significance, which in its own field belongs to Planck's constant h.

As a result of relationship (4) we have:

$$\Delta\Phi_s \Delta X_\mu \approx 2\pi r_{s\mu}. \tag{5}$$

In other words, if $\Delta X_\mu \approx r_{s\mu}$ the phase becomes altogether indeterminate:

$$\Delta\Phi_s \approx 2\pi. \tag{6}$$

We determine vector $r_{s\mu}$ in the following manner:

$$2\pi r_{s\mu} = b k_{s\mu} \tag{7}$$

where $K_{s\mu}$ is a four-dimensional wave vector:

$$k_{sx},\ k_{sy},\ k_{sz},\ i\,|\bar{k}_s|;$$

b is factor of proportionality, whose dimension is square of length. As a consequency of relations (4) and (7) we have:

$$e^{\mp i\Phi_s} \cdot f(\bar{r}) = f(\bar{r} \mp i b \bar{k}_s)\, e^{\mp i\Phi_s}. \tag{8}$$

For instance:

$$\left.\begin{aligned} N_s^+ \cdot e^{i\bar{k}_s\bar{r}} &= e^{-bk_s^2} \cdot e^{-i\bar{k}_s\bar{r}} \cdot N_s^+, \\ N_s^- \cdot e^{+i\bar{k}_s\bar{r}} &= e^{-bk_s^2} \cdot e^{+i\bar{k}_s\bar{r}} \cdot N_s^-. \end{aligned}\right\} \tag{9}$$

It will be easily seen from (4) that operator Φ_s could be written in the form:

$$\Phi_s = -i\frac{\partial}{\partial n_s} + 2\pi r_{s\mu}\frac{\partial}{\partial k_\mu}. \tag{10}$$

Special attention is called to the fact that in the theory developed by us we find the natural appearance (9) of cutting off factor:

$$e^{-bk_s^2}. \tag{11}$$

From relation (7) it follows that factor b is a constant whose dimension is square of length.

Let

$$b = (2\pi r_0)^2. \tag{12}$$

Let us examine, as a particular case of the theory of field here evolved, Maxwell's field, i. e. quantum electrodynamics.

a) Longitudinal Self-Energy of the Electron

If in conformity with (4) (i. e. bearing in mind that $N_s^{\pm} e^{-\frac{iEt}{\hbar}} = e^{\mp\frac{bk_sE}{\hbar c}}\ e^{-\frac{iEt}{\hbar}} N_s^{\mp}$) we pass over from equation

$$H\psi - ih\frac{\partial\psi}{\partial t} = -\{e_1\varphi(r_1) + e_2\varphi(r_2)\}\psi \tag{13}$$

to stationary equation [$\varphi(r)$ is scalar potential], then we shall obtain in the usual way for the electrostatic energy of the electron the expression:

$$W_{\text{long}} = \frac{1}{2\pi^2}\frac{e^2}{hc}\int\int \varphi^+(\bar{k}')\,\frac{e^{-i\bar{k}'\bar{r}}\cdot\varphi^-(\bar{k})}{k}\cdot e^{+i\bar{k}\bar{r}}\,d\bar{k}\,d\bar{k}'. \tag{14}$$

In its outer appearance this expression differs in nothing from the corresponding expression of ordinary theory.

But on account of (9):

$$\varphi^+(k')\,e^{-i\bar{k}'\bar{r}} = e^{-bk'^2}\cdot e^{-i\bar{k}'\bar{r}}\,\varphi^+(k').$$

Since the oscillators of the field are not excited ($n_s = 0$), we have:

$$\varphi^-(k)\,\varphi^+(k') = 0;\quad \varphi^+(k')\,\varphi^-(k) \approx \frac{ch}{2k'}\,\delta(k'-k).$$

In result of the above we have:

$$W_{\text{long}} = \frac{e^2}{\pi}\int_0^\infty e^{-bk^2}\,dk,$$

$$W_{\text{long}} = \frac{e^2}{4(\pi)^{\frac{3}{2}}}\cdot\frac{1}{r_0}. \tag{15}$$

b) Transverse Self-Energy of the Electron (1)

Calculating the mean value of term $\frac{1}{2m}\frac{e^2}{c^2}A^2$ (where A is vector potential) in Schrödinger's equation (or the second approximation in Dirac's theory) we obtain:

$$W_{\text{trans}}=\frac{1}{2\pi^3}\frac{e^2}{2mc^2}\int\int\{A^+(k')\cdot e^{-i\bar{k}\bar{r}}\cdot A^-(k)\,e^{+i\bar{k}\bar{r}}+ \\ +A^-(k')\cdot e^{+i\bar{k}'\bar{r}}A^+(k)\,e^{-i\bar{k}\bar{r}}\}\,d\bar{k}\,d\bar{k}'.$$

Further, according to (9):

$$W_{\text{trans}}=\frac{1}{2\pi^2}\frac{e^2}{2mc^2}\int\int e^{-bk'^2}[A^+(k')\,A^-(k)+A^-(k')\,A^+(k)]\,d\bar{k}\,d\bar{k}'.$$

And if in the field there are no other photons but «zero» photons, then:

$$A^+(k')\,A^-(k)+A^-(k')\,A^+(k)=\delta(k-k')\,\frac{\hbar c}{2k'}$$

consequently:

$$W_{\text{trans}}=\frac{e^2\hbar}{2\pi mc}\int_0^\infty e^{-bk^2}k\,dk=\frac{\hbar e^2}{mc}\cdot\frac{1}{8\pi^3}\cdot\frac{1}{r_0^2} \qquad (16)$$

with

$$r_0\sim\frac{e^2}{mc^2};\quad W_{\text{trans}}\sim mc^2,$$

i. e. the origin of the self-mass of the electron is on the main due to zero fluctuations of the oscillators of the field. The electrostatic mass of the electron will in this case be found to be several times less than the transverse one.

The latter instance appears to be of particular interest on account of the fact that the corresponding divergent expression of ordinary theory ($\int k\,dk$) is connected, as is well known (2), with zero fluctuations of the oscillators of the field.

The statements made so far bear essentially a prescriptive character, i. e. we have proposed to take Dirac's equations with field quantized in the ordinary manner and then to superimpose conditions (4).

But quantum electrodynamics evolved in the works of Heisenberg, Pauli and others represents in certain sense a consecutive transition from the classical theory of field to the quantum theory.

Therefore it is desirable in the theory here developed to carry out this transition in as consecutive a way as in the former theory.

It appears possible, bearing in mind conditions (4), to repeat at full length Heisenberg-Pauli's scheme; to obtain, for instance, relation (2), etc.

But, in this case, we have to take into consideration the fact that besides operators E and H there are also «adjungierte» expressions non-identical to them:

$$E\neq E^+;\quad H\neq H^+.$$

On account of this it will be possible by applying Lagrange's classical function to compare formally two quantum expressions:

$$L'=\frac{1}{8\pi}(E^2+H^2);\quad L''=\frac{1}{8\pi}(E\cdot E^+-H\cdot H^+).$$

All the above stated is associated with the selection of function L''. (The choice of L' in capacity of Lagrange's function entails an unusual connexion between frequency and photon energy).

c) Measurements

Conditions (4) lead, evidently, to further serious changes in our conceptions of space and time.

Indeed, the most perfect—the interferential—method for measuring lengths within small regions of space becomes devoid of any kind of sense, since phase differences become altogether indeterminate.

This circumstance imposes, however, to all appearance, no restrictions whatever upon the measurement of the impulse of particles (the photon, the electron, etc.). In other words, in a small space-time range the theory becomes deprived of its wave character and the corpuscular properties of particles begin again to preponderate in the aforesaid sense.

Conditions (4) all impose certain restrictions upon the mesurability of the field-strength. «Individual» errors in measurements of the field-strength are likely to make their appearance [3].

For instance, for a longitudinal electric field we obtain:

$$\overline{E}_{\text{long}}\overline{r} - \overline{r}\overline{E}_{\text{long}} > r_0 E_{\text{long}},$$
$$\Delta E_{\text{long}} \Delta r > r_0 E_{\text{long}}$$

with

$$\Delta r \sim r_0$$
$$\Delta E_{\text{long}} > E_{\text{long}}$$

i. e. at the «edge» of the electron field magnitude (E_{long}) is totally indeterminate.

The theory evolved here is not a single-sign construction, since we have arbitrarily chosen the simplest rules of commutation.

For instance, in capacity of phase operator it will be possible, instead of operator $2\pi r^0_{s_\mu} \frac{\partial}{\partial X_\mu}$, to take any functions of the invariant combinations of two four-dimensional vectors k_μ and $\frac{\partial}{\partial X_\mu}$.

Another most important point where the developed theory may encounter serious difficulties is the field of cosmic rays.

P. N. Lebedev Physical Institute.
Academy of Sciences of the USSR.

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PHYSICS

ON THE MAGNETRON CUT-OFF CURVE

By G. V. SPIWAK and P. E. ZREBNY

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The energy of the random motion of electrons in a magnetron is usually supposed to be determined by the temperature of the cathode (1). It was pointed out by Langmuir, however, as early as 1925, that the currents to an additional electrode introduced in the magnetron tend to take considerable values. The latter proved great in that case, too, when the electrode was made strongly negative and there were no electrical oscillations in the magnetron. Those effects in the presence of a magnetic field exceeding the critical one were thoroughly investigated by Wigdortschic (3), who found the electrons to move with Maxwellian velocity distribution which corresponded to a temperature running into tens of electronovolts. The fact that the magnetic field is liable to set up high temperature Maxwellian distribution of velocities can easily be understood if the interaction between the electrons is considered, owing to which part of the energy supplied by the accelerating field turns into a random one. The rôle of the magnetic field as a factor decreasing the current is only to lengthen the transit time of the electrons and to increase the density of space discharges. With the exception of (4) nobody appears to have made an attempt at expressing the equation for the cut-off curve of the magnetron by considering the random velocity as a function of magnetic field. Such an expression can be derived, however, if the temperature of the electronic gas is supposed to be high; yet as obtained by Linder (4) it is incorrect, because there is a substantial error in his method of calculation.

From the equation of electron motion we can arrive, by making good use of a method described formerly (5), at a relation connecting the components of the random velocity with the parameter of the problem. Only those electrons reach the anode of the magnetron which satisfy the condition:

$$u^2+\left(1-\frac{r_0^2}{R_0^2}\right)\frac{\varepsilon^2}{4m^2}\left\{\left(Hr_0-\frac{2mv}{\varepsilon}\right)^2-R_0^2H^2\right\}+2\frac{\varepsilon}{m}\varphi\geqslant 0, \qquad (1)$$

where u, v, ε, m are radial, tangential components of the random velocity, charge and mass of the electron respectively; r_0, R_0 are radii of the cathode and anode of the magnetron; H and φ are magnetic field and anode potential. Relation (1) is obtained on the assumption that φ is zero

on the cathode, and that with $r=r_0$ the velocity of the electron is given by the components u and v. If $R_0 \gg r_0$ it follows from (1) that

$$u^2+v^2-\frac{R_0^2H^2\varepsilon^2}{4m^2}+2\frac{\varepsilon}{m}\varphi \geqslant 0. \qquad (2)$$

Here u and v enter symmetrically into the formula. Substituting $u^2+v^2=c^2$ into this equation we see that two cases are possible:

$$1)\ \varphi>0 \quad \text{but} \quad 2\frac{\varepsilon}{m}\varphi>\frac{R_0^2H^2\varepsilon^2}{4m^2}$$

and

$$2)\ \varphi>0 \quad \text{but} \quad 2\frac{\varepsilon}{m}\varphi<\frac{R_0^2H^2\varepsilon^2}{4m^2}$$

or $\varphi<0$ or else can assume arbitrary values.

In the first case the electrons hit the anode whatever may be the value of c, while in the second case they do so only under the condition that

$$c \geqslant \sqrt{\frac{R_0^2H^2\varepsilon^2}{4m^2}-2\frac{\varepsilon}{m}\varphi}.$$

If the electrons obey Maxwell's distribution law, the function of distribution expressed in cylindrical co-ordinates will take the form:

$$f(c,\omega)=2\pi c' e^{-\alpha(c^2+\omega^2)}\,cdcd\omega$$

and the expression for the current is

$$I=2\pi c'\varepsilon\int_{c_1}^{\infty} e^{-\alpha c^2}c^2dc\int_{-\infty}^{+\infty} e^{-\alpha\omega^2}d\omega \qquad (3)$$

where

$$c_1=\sqrt{\frac{R_0^2H^2\varepsilon^2}{4m^2}-2\frac{\varepsilon}{m}\varphi},$$

the constant $\alpha=\frac{m}{(2kT)}$. Integrating from 0 to ∞ with respect to c and from $-\infty$ to $+\infty$ with respect to ω will determine c'. The integration of (3) gives

$$I=I_S\left[1+\frac{2}{\sqrt{\pi}}\sqrt{\xi^2R_0^2-\eta}\,e^{-(\xi^2R_0^2-\eta)}-P\left(\sqrt{\xi^2R_0^2-\eta}\right)\right] \qquad (4)$$

where

$$\xi=\frac{\varepsilon H}{\sqrt{8mkT}}, \qquad \eta=\frac{\varepsilon\varphi}{kT},$$

$$P(x)=\frac{2}{\sqrt{\pi}}\int_0^x e^{-y^2}dy,$$

k is Boltzmann's constant, I_S is current in the magnetron at $H \leqslant H_c$ (H_c cut-off value of the magnetic field); (4) is an analytical expression for the magnetron characteristics. It holds true, as is seen from the consideration of the 1st and the 2nd case, where $\eta>0$, provided that $\eta<\xi^2R_0^2$, while with $\eta<0$ no restriction whatever is placed upon the values η and ξ.

From the definition of the cut-off value of the magnetic field H_c ensues the equality $H_c=\sqrt{\frac{8m}{\varepsilon}\frac{\varphi^{\frac{1}{2}}}{R_0}}$. In our notation we find the values ξ_c and η to be related with each other by the equation

$$\xi_c^2R_0^2=\eta. \qquad (5)$$

Introduction of (5) into (4) yields an expression for the current as a function of $\xi^2 - \xi_c^2$:

$$I = I_S \left[1 + \frac{2R_0}{\sqrt{\pi}} \sqrt{\xi^2 - \xi_c^2}\, e^{-R_0^2(\xi^2 - \xi_c^2)} - P\left(R_0 \sqrt{\xi^2 - \xi_c^2}\right) \right]. \qquad (6)$$

From (6) it is evident that $I = I_S$ with $\xi = \xi_c$ and that $I = 0$ with $\xi \gg \xi_c$. (6) shows that the magnetron characteristic can easily be plotted as a function of H^2. This plot is represented in Fig. 1 for $\frac{R_0}{\sqrt{T}} = 4.9 \cdot 10^{-3}$. $\ln \frac{I}{I_S}$ is plotted along the axis of ordinates; $\frac{H^2}{100}$ along the axis of abscissae.

When $\xi - \xi_c$ is small, the current goes down more slowly than according to exponential law. But it practically follows the latter after this difference has become great. The solution of the problem has of late been obtained by Linder ([4]) in the form:

$$I_p = I_1 e^{-\left(\frac{m}{2kT}\right)\left(\frac{re}{2m}\right)^2 (H_c^2 - H^2)}, \qquad (7)$$

or, expressed in the symbols accepted here

$$I = I_S e^{-R_0^2(\xi^2 - \xi_c^2)}. \qquad (7')$$

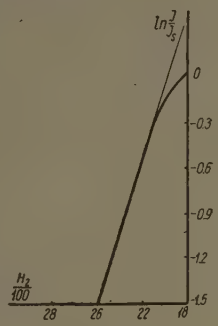

Fig. 1.

There is a considerable departure in the relation obtained by Linder (7′) from our formula (6). With small $\xi - \xi_c$ the decrease in current proceeds differently in (7′) from as it does in (6). With great $(\xi - \xi_c)$ the difference will arise on account of the factor $\frac{2}{\sqrt{\pi}} R_0 \sqrt{\xi^2 - \xi_c^2}$ entering into formula (7′). The discrepancy between (6) and (7′) is due to an error admitted by Linder in calculating the density of the current. The density of the electron swarm near the emitter multiplied by the velocity of the electrons near the anode fails to give the density of the current which he believed himself to have obtained in that way.

Two methods may serve to verify the correctness of our solution. Putting $\xi = 0$ in (4) we obtain the relation

$$I = I_S \left[1 + \frac{2}{\sqrt{\pi}} \sqrt{-\eta}\, e^{\eta} - P\left(\sqrt{-\eta}\right) \right] \qquad (8)$$

which for $\eta < 0$ fits in with the formula derived by Schottky ([6]). Linder's formula refuses to yield the expression (8) and this also goes to disprove his result.

An interesting point to note here is that (6) reflects the characteristic features of the experimental curves. If the values for $\ln \frac{I}{I_S}$ obtained experimentally by Hull [([1]), p. 44, fig. 8] and Linder [([4]), p. 332 and 333, Fig. 2 and 3] be plotted against H^2, the shape of the curves will be as it is in Fig. 1.

Essential is that the straight parts of the curves have their angle of inclination changing with φ which fact is related to an increase in electron temperature T. Given H_c grows with φ; the rise of the temperature can also be brought in connexion with H_c. If $\varphi = 200$ volt the experimental curve in Fig. 3 (p. 333) of the paper cited ([4]) strongly deviates from a straight line which should be in accord with Linder's theoretical considerations.

Let us proceed now to a quantitative comparison of the formula (6) and the observation. Best agreement should be expected with small values of $\xi - \xi_c$, since in deriving the formula no allowance was made for the appearance of minimum potential between the electrodes, and the space was considered only slightly saturated with negative space charges.

Taking into account two terms of (6) for the exponential function and for the error integral, from the expansion of (7) one can, if $\xi \geqslant \xi_c$, write:

$$I = I_S\left[1 - \frac{4R_0^3}{3\sqrt{\pi}}(\xi^4 - \xi_c^2)^{\frac{3}{2}}\right]. \qquad (9)$$

Analyzing this expression we see that $\frac{I_S - I}{I_S}$ should be a linear function of $(H^2 - H_c^2)^{\frac{3}{2}}$ and have the tangent of its inclination angle equal to $\frac{\varepsilon^3 R_0^3}{[12\sqrt{2\pi}(mk)^{\frac{3}{2}} T^{\frac{3}{2}}]}$. If these characteristics are plotted (Fig. 2) on the basis of the experimental data obtained by Hull (Fig. 8, p. 44), they prove to be linear in their lower part in accordance with (9). The change

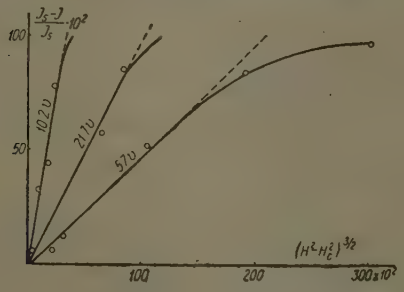

Fig. 2.

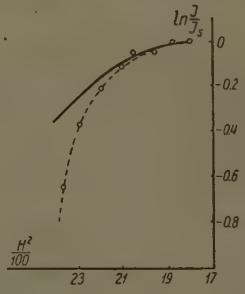

Fig. 3.

in the inclination angle of the straight part of the characteristic is related to the change in electron temperature. By determining the value $\frac{R_0}{\sqrt{T}}$ from this inclination (Fig. 2) for the case when $\varphi = 57$ volts and substituting it into (6) we are able to plot the dependence of $\ln \frac{I}{I_S}$ upon H^2, as it has been done in Fig. 3. Here the theoretical curve is drawn as a full line while the dotted line is the experimental curve. Both curves are running sufficiently close to each other at small values of H^2. However, as the magnetic field grows the decrease in the current becomes stronger than that indicated by relation (6). The deviation is due to the action of space charges.

The existence of a relation between the anodic current and the space charges has been noted by Bellustin ([8]). Tonks ([9]) while discussing the results reported by Braude ([10]) has pointed toward the fact that the current in a magnetron should start decreasing when the values of magnetic field are below the cut-off point. The reason of this lies in the presence of negative space charges. The same conclusion was reached by Grinberg and Wolkenstein ([11]). The point from which one starts to obtain this result is the supposition that before the magnetic field is switched in

the space is already saturated with space charges (the field near the cathode $E=0$). Naturally enough, this condition is not realized (near the cathode $E>0$) until after the voltage on the anode has become sufficiently small. It will be obvious that it is a case when our calculation should be in good agreement with the experiment (Fig. 3). But as soon as $H \gg H_c$, a linear dependence of $\ln \frac{I}{I_S}$ upon H^2 is required by formula (6). The experiments of Linder (Fig. 3, p. 333) confirm this run of the curve.

The reason for the exponential drop of the current when H is not too great seems to lie in the appearance of minimum potential with additional selection of electrons taking place here through the agency of the retarding electrical field.

From the good quantitative agreement with observation obtained by us (Fig. 3) for the case of small $H-H_c$ it is evident that we must take account of the high random energy of the electrons while developing further the theory which considers the space charges and the presence of oscillations.

This peculiar nature of the magnetron is typical not only for the static condition, but it appears to be the principal factor in the dynamic condition as well.

Laboratory of Electronic and Ionic Processes.
Physical Institute.
Moscow State University.

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PHYSICS

INFLUENCE OF MAGNETIC FIELD UPON ELECTRON MOTION IN AXIALLY SYMMETRICAL FIELDS

By G. V. SPIWAK and P. E. ZREBNY

(Communicated by S. I. Wawilow, Member of the Academy, 26. V. 1939)

1. Dealing with the problems which concern the electron motion inhibited by the influence of an electric field, leads us to the necessity of taking into account the initial velocities of the electron ([1],[2]). If the electrons moving in accelerating fields are under the action of a magnetic field too, the calculation of the current, beginning with certain values of H, cannot be made properly when the random motion of the electrons is neglected ([3],[4]).

An important point to note here is that the currents between two co-axial cylinders are not indifferent to the fact whether it is the electrode with the greater or that with the smaller radius which emits electrons.

The factor responsible for this variation of currents is the tangential component v which plays a different rôle in these two cases.

According as the electrons are emitted by the outer electrode with radius R_0 [case a] or by the electrode with radius r_0 [case b] there is a different kind of relation between the velocity components u and v of the electrons transferring the current, on the one hand, and the parameter of the problem, on the other:

$$\text{case a)}\quad u^2 - v^2\left(\frac{R_0^2}{r_0^2} - 1\right) + 2\frac{\varepsilon}{m}\varphi \geqslant 0, \tag{1}$$

$$\text{case b)}\quad u^2 + v^2\left(1 - \frac{r_0^2}{R_0^2}\right) + 2\frac{\varepsilon}{m}\varphi \geqslant 0, \tag{2}$$

when φ is negative potential on the collecting electrode, ε, m and u are charge, mass and normal velocity component of the electrons, respectively. From these relations it is evident that in the case a) tangential component hinders the electrons, while in the case b) it helps them to reach the electrode. This is brought out in Fig. 1 when v expressed as function of u has taken its ultimate values which are determined by the relations:

$$v = \pm\sqrt{\vartheta^2\lambda\left(u^2 + 2\frac{\varepsilon}{m}\varphi\right)} \tag{1'a}$$

and

$$v = \pm\sqrt{\lambda\left(-u^2 - 2\frac{\varepsilon}{m}\varphi\right)}, \tag{2'b}$$

deriving from (1) and (2) for the case when the latter present equalities; whereby $\vartheta = r_0/R_0$ and $\lambda = 1(1-\vartheta^2)$. The least value

$$u_c = \sqrt{-2\frac{e}{m}\varphi}. \tag{3}$$

It will be apparent that (1'a) determines the two greatest values of v while two least values are determined by (2'b).

The hatching on the left-hand side of Fig. 1 indicates the prohibited zone for the case b) while that on the right-hand side refers to the case a) when the electrons hit the electrodes. These two regions have a common point determined by condition (3). The drawing is made on the assumption that $\vartheta = \frac{1}{2}$, $\varphi = -32$ volts. As is seen from this figure the electrons captured in the case a) and in the case b) have different velocities and, therefore, the currents will be different, too. At $R_0 \gg r_0$

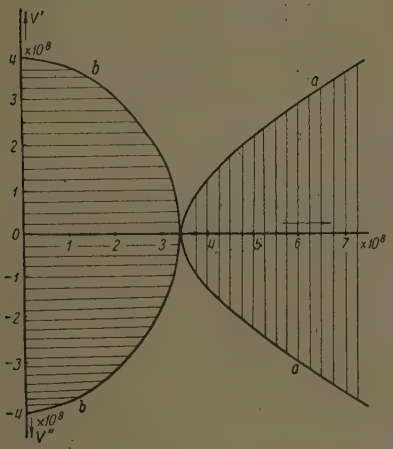

Fig. 1.

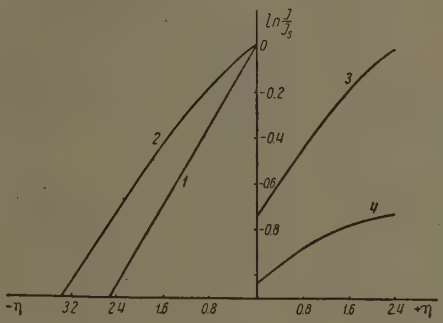

Fig. 2.

the left region is a semi-circle. If a homogeneous magnetic field is applied along the axis of the cylinder, the conditions (1'a) and (2'b) change into:

$$v = \frac{eHR_0}{2m} \pm \sqrt{\vartheta^2\lambda\left(u^2 + 2\frac{e}{m}\varphi\right) + \frac{e^2r_0^2H^2}{4m^2}}, \tag{1''a}$$

$$v = \frac{eHr_0}{2m} \pm \sqrt{\frac{e^2R_0^2H^2}{4m^2} - \lambda\left(u^2 + 2\frac{e}{m}\varphi\right)}. \tag{2''b}$$

Relation (2''b) is derived from formula (1) of the preceding paper [4], (1''a) has been obtained formerly [3].

These relations show that the effect of magnetic field is to change the position and dimensions of the regions marked out in Fig. 1. The prohibited zone b becomes wider, while a is shifted toward the left and upward. Detailed analysis shows that a decrease in currents is the invariable result of those changes.

In order to illustrate the asymmetry of the currents in the cases a) and b) the respective curves are presented in Fig. 2, drawn on a semi-logarithmic scale for $R_0 \gg r_0$. The left is the case of negative η and

$\xi=0$, the right is that of positive η and $\xi^2R_0^2=2.4$. The curves obey the equations

$$\left.\begin{aligned} &I=I_S e^{\eta} && \text{(curve 1)},\\ &I=I_S\left[1+\frac{2}{\sqrt{\pi}}\sqrt{-\eta}\,e^{\eta}-P\left(\sqrt{-\eta}\right)\right] && \text{(curve 2)},\\ &I=I_S\left[1+\frac{2}{\sqrt{\pi}}\sqrt{\xi^2R_0^2-\eta}\,e^{-(\xi^2R_0^2-\eta)}-P\left(\sqrt{\xi^2R_0^2-\eta}\right)\right] && \text{(curve 3)},\\ &I=I_S e^{-\xi^2R_0^2}\left\{\frac{2}{\sqrt{\pi}}\sqrt{\eta}+e^{\eta}\left[1-P\left(\sqrt{\eta}\right)\right]\right\} && \text{(curve 4)}. \end{aligned}\right\} \quad (4)$$

It will be obvious that whether the magnetic field is switched or not the currents are always greater in the case b) than they are in the case a), owing to the effect produced by the tangential component of the initial velocity.

2. In the preceding paper [4] we were discussing the case of electrons moving in a magnetron when the magnetic field exceeds its critical value. This was being done on the assumption that $R_0 \gg r_0$. The supposition implies that the tangential component assumes its ultimate value determined from the expression

$$v=\pm\sqrt{\frac{\varepsilon^2R_0^2H^2}{4m^2}-\left(u^2+2\frac{\varepsilon}{m}\varphi\right)}. \quad (5)$$

The solution obtained does not hold true for any value of ϑ, because then the condition (5) must be replaced by (2″b). The main object of the present paper is to obtain a more general solution which will embrace the case of arbitrary relation between the radii of the cylinder R_0 and r_0.

The critical value of u_c is determined by the condition under which the radical term of (2″b) turns to zero:

$$u_c=\sqrt{\frac{\varepsilon^2H^2}{4m^2}(R_0^2-r_0^2)-2\frac{\varepsilon}{m}\varphi}. \quad (6)$$

If $u>u_c^a$, the electron will reach the collecting electrode whatever may be its tangential component. But with $u<u_c$ only those electrons can be caught whose tangential components exceed the values yielded by (2″b).

Subtracting the electrons which fail to hit the electrode from the number of emitted electrons we obtain:

$$I=I_S-\frac{2}{\sqrt{\pi}}I_S\int_0^{\sqrt{\xi^2(R_0^2-r_0^2)-\eta}}e^{-x^2}x\,dx\int_{y'}^{y''}e^{-y^2}\,dy. \quad (7)$$

Here as in (4), when the same notation is used, the electrons are supposed to obey Maxwell's distribution law. The upper limit of x has been obtained from (6), while the limits of y as determined from (2″b) take the form:

$$y'',y'=\xi r_0\pm\Omega. \quad (8)$$

The multiple integral in (7) multiplied by $-\frac{\sqrt{\pi}}{2-I_S}$ and after integration by parts turns into:

$$\frac{1}{2}\int_{\xi r_0-f(\xi,\eta)}^{\xi r_0+f(\xi,\eta)}e^{-y^2}dy-\frac{\lambda}{2}\left[\int_0^{\sqrt{\xi^2(R_0^2-r_0^2)-\eta}}\frac{1}{\Omega}e^{-\psi_1}x\,dx+\int_0^{\sqrt{\xi^2(R_y^2-r_0^2)-\eta}}\frac{1}{\Omega}e^{-\psi^2}x\,dx\right], \quad (9)$$

where

$$\psi_{1,2} = x^2 + (\xi r_0 \pm \Omega)^2,$$
$$\Omega = \sqrt{\xi^2 R_0^2 (x^2+\eta)\lambda},$$
$$f(\xi,\eta) = \sqrt{\xi^2 R_0^2 - \eta\lambda}.$$

$\psi_{1,2}$ may be written as:

$$\psi_{1,2} = \left(r_0 \sqrt{\xi^2 - \frac{x^2+\eta}{R_0^2 - r_0^2}} \pm R_0 \xi \right)^2 - \eta.$$

After this value is substituted in (9) we replace the variable x by the variable

$$y = r_0 \sqrt{\xi^2 - \frac{x^2+\eta}{R_0^2 - r_0^2}} \pm R_0 \xi$$

to obtain (9) in the form:

$$\frac{1}{2} \int_{\xi r_0 - f(\xi,\eta)}^{\xi r_0 + f(\xi,\eta)} e^{-y^2} dy + \frac{e^\eta}{2\vartheta} \left(\int_{f(\xi,\eta)+R_0\xi}^{R_0\xi} e^{-y^2} dy + \int_{f(\xi,\eta)-R_0\xi}^{-R_0\xi} e^{-y^2} dy. \right. \tag{9'}$$

With this expression introduced in (7) we have, if $\eta < 0$:

$$I = I_S \left\{ 1 - \frac{1}{2} \left[P\left(\sqrt{\xi^2 R_0^2 - \eta\lambda} + \xi r_0\right) + P\left(\sqrt{\xi^2 R_0^2 - \eta\lambda} - \xi r_0\right) \right] + \right.$$
$$\left. + \frac{e^\eta}{2\vartheta} \left[P\left(\vartheta \sqrt{\xi^2 R_0^2 - \eta\lambda} + R_0 \xi\right) \mp P\left(\mp \vartheta \sqrt{\xi^2 R_0^2 - \eta\lambda} \pm \xi R_0\right) \right] \right\}, \tag{10}$$

whereby

$$P(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-y^2} dy.$$

Whether the upper or the lower sign must be taken in (10) is determined by

$$-\eta \vartheta^2 \lambda^2 \gtrless \xi^2 R_0^2.$$

With $\xi \to \infty$ in (10), $I \to 0$, while with $\xi \to 0$ we have

$$I = I_S \left[1 - P\left(\sqrt{-\eta\lambda}\right) + \frac{e^\eta}{\vartheta} P\left(\vartheta \sqrt{-\eta\lambda}\right) \right], \tag{11}$$

and this expression fits in with the formula derived by Schottky [1].

It is a simple matter to show that (10) is properly reduced to the limiting case $R_0 \gg r_0$ even if $\xi \neq 0$.

If ξr_0, which is too small compared to $\pm f(\xi,\eta)$, is neglected in the first integral of (9') and in the third and the second integrals the variable y is replaced by a new one $y = \vartheta x \pm R_0 \xi$, we have:

$$\int_0^{\sqrt{\xi^2 R_0^2 - \eta}} e^{-y^2} dy - \frac{1}{2} e^{-(\xi^2 R_0^2 - \eta)} \left[\int_0^{\sqrt{\xi^2 R_0^2 - \eta}} e^{-(\vartheta^2 x^2 + 2\vartheta R_0 \xi x)} dx + \right.$$
$$\left. + \int_0^{\sqrt{\xi^2 R_0^2 - \eta}} e^{-(\vartheta^2 x^2 - 2\vartheta R_0 \xi x)} dx \right], \tag{9''}$$

with $\vartheta \to 0$ $\vartheta^2 x^2$ and $\pm 2\vartheta R_0 \xi x$ tend to zero as well. Multiplying (9'') by $-\frac{2I_S}{\sqrt{\pi}}$ and adding I_S, we obtain, according to (7), the expression (4) for the current.

This relation was obtained by us formerly in another way [4].

The expression analogous to (10) which is obtained from (7) when $\eta > 0$ is

$$I = I_S\left\{1 - \frac{1}{2}\left[P\left(\sqrt{\xi^2 R_0^2 - \eta\lambda} \pm \xi r_0\right) \mp P\left(\mp\sqrt{\xi^2 R_0^2 - \eta\lambda} + \xi r_0\right)\right] + \right.$$
$$\left. + \frac{e^{\eta}}{2\vartheta}\left[P\left(\xi R_0 + \vartheta\sqrt{\xi^2 R_0^2 - \eta\lambda}\right) - P\left(\xi R_0 - \vartheta\sqrt{\xi^2 R_0^2 - \eta\lambda}\right)\right]\right\}. \quad (10')$$

According as $\eta\lambda^2 > \xi^2 R_0^2$ is greater or smaller than $\eta\lambda^2 < \xi^2 R_0^2$ we take the upper or the lower height in (10').

This expression holds true until

$$\xi^2 (R_0^2 - r_0^2) \geqslant \eta. \quad (12)$$

With this the cut-off value of the magnetic field is determined as

$$H_c = \sqrt{\frac{8m}{e} \frac{\varphi^{1/2}}{R_0^2 - r_0^2}}. \quad (12')$$

From (10') it is evident that as soon as the condition (12) is fulfilled, the effect of the magnetic field is to decrease I which with $\xi \to \infty$ tends to zero.

As noted by Tonks [5] the decrease in the current may sometimes take place with $H < H_c$ and is then due to the action of the space change. This circumstance can be disregarded if η is negative and has its least value at $r = R_0$. But with $\eta > 0$ such conditions are possible when we cannot dispense with making allowance for the decrease in the current at $H < H_c$.

The formulae obtained may be used in computing the currents to the wall of a discharge tube [6] as well as for calculation of processes taking place in a magnetron when a virtual cathode is available.

Department of Theoretical Physics.
K. Libknecht Pedagogical Institute.
Moscow.

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PHYSICS

HALL EFFECT IN PLASMA

By M. I. RODIN and G. V. SPIWAK

(Communicated by S. I. Wawilow, Member of the Academy, 26. V. 1939)

The investigations devoted to the influence of a crossed magnetic field upon a gaseous discharge have chiefly dealt with the qualitative side of this phenomenon. There are some observations on the influence of a crossed field upon the plasma made with probes by Langmuir and Mott-Smith (1), but neither the quantitative data on the Hall effect produced by magnetic field nor the distribution curves for the electron concentration along the radius of the discharge tube have been reported by these authors.

In previous works carried out at our laboratory (2–5) there was developed a method for studying the discharge in a magnetic field. It was thereby found that the effect of the latter is to change the conditions under which the electron can reach the probe. The fact that the indications given by the probe are liable to change in that way is of special significance when the potential of the probe is near to the space potential. Great errors are apt to arise from disregard of this circumstance, because it is at the space potential that the probe records which serve to determine the concentration of electrons are made (3). Thorough experiments with weak magnetic fields were performed by Fataliev (4) and he was able to demonstrate the presence of these distortions. Our choice of the gas pressure, the form and position of the probe was directed by the aim to reduce the distortion in the upper parts of the probe characteristics (due to the effects in the neighbourhood of the probe) to a minimum.

For argon, neon and mercury vapour we have studied the change in electron concentration along the radius of a cylindrical discharge tube, have determined the cross potential difference and traced the run of potential gradient in a crossed magnetic field. The measurements were made with varying currents and pressures.

While they were being done in mercury vapour, the entire tube was placed in a thermostat. With weak currents in the side branch (fractions of one ampere) the mercury vapour pressure corresponding to the temperature of the branch wall was determined by the conditions of the thermostat. The branch, in which the measurements were carried on, was about 65 cm long and 3.5 cm in diameter. Two cylindrical probes were sealed in perpendicular to the branch axis and 6 cm apart from each other. Between them two plane probes were placed, in close contact with the two opposite walls. 4 cm apart from the second cylindrical probe a third plane probe was introduced which was free to move along the radius of the tube and about its own axis.

The first pair of probes served to measure the longitudinal potential gradient on the basis of the current compensation between them. This method, however, will not yield reliable results unless the two probes are under equal conditions in the discharge. Therefore, the magnetic field was adjusted symmetrically with respect to both probes when the gradient was being measured.

The two opposite probes in contact with the wall served to measure the transverse potential difference, which arises from switching in the magnetic field.

The movable plane probe recorded the change in electron density across the discharge.

The crossed magnetic field was generated by two Helmholtz coils between which the branch of the flask was located. The field was sufficiently homogeneous; its maximum value amounted to 150 gauss.

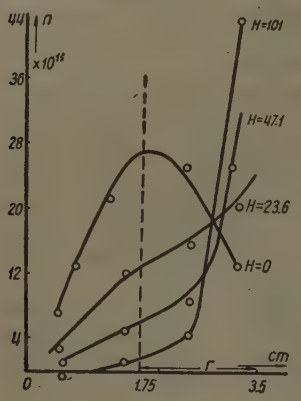

Fig. 1.

Fig. 1 shows the electron concentration across the tube, which varies with the co-ordinate. The parameter of the curve is the magnetic field. The curve corresponding to the case when $H=0$ gives the distribution of the concentration in undisturbed plasma. This curve is not quite symmetrical with respect to the tube axis (dotted straight line) because of plasma being distorted by the wall canal along which the probe travels. In one half of the tube the density of the electron swarm drops abruptly with the increase of magnetic field, while in the other half it rises considerably. Finally the entire discharge in the space between the coils is pressed to one side of the tube, and is eventually damped unless the voltage on the tube is made to increase. During the measurements the current in the side branch of the flask, i. e. in the mercury vapour, was kept equal to 0.2 amperes; the pressure of the mercury vapour was about 0.2 mm. All of the curves in Fig. 1 were obtained from the characteristics of the probe when its plane was perpendicular to the magnetic field. The control measurements were made with the same probe, but with its operating plane directed parallel to the field. The distortions in the upper parts of probe characteristics were estimated at a given pressure of the mercury vapour.

It is worthy of note that even if the plasma is rather strongly disturbed by a crossed field the probe characteristics do not exhibit any considerable departure from Maxwell's distribution law. With the magnetic field applied the longitudinal gradient in the plasma increases, as it was to be expected, indeed.

And not only the phenomena within the volume but the conditions on the wall as well are changed by the magnetic field. One of the chief reasons which may be put forward to account for the increase in gradient is that the discharge is pressed to the wall and the result is a loss in the number of charged particles.

Within the range of magnetic fields tested and the pressures varying between 0.01 and 0.4 mm the gradient grew with the field almost linearly.

In longitudinal fields the variation of the gradient is governed by a different law [5].

Fig. 2 shows the cross potential difference of the Hall effect measured in a tube filled with mercury vapour at a pressure of 0.01 mm for a current of

0.1 A (curve *1*) and 0.2 A (curve *2*). The potential difference grows at first linearly and then tends to saturation. These data were yielded both through a compensation to zero of the current between the two opposite probes and otherwise.

The left side of Fig. 2 shows the potential of the probe touching the wall to vary as a function of the magnetic field.

The upper *1*, *2*, *3* and the lower *1′*, *2′*, *3′* curves apply to the probe from which and to the probe toward which the discharge is moving, respectively.

The potential of each of those probes with reference to the anode was determined on the assumption that the current to the probe was zero.

The cross potential difference found in that way differed but slightly from that obtained by the method of direct compensation of the current between the probes.

The curves *1*, *2*, *3* and *1′*, *2′*, *3′* correspond to currents of 0.1, 0.2 and 0.3 A, respectively.

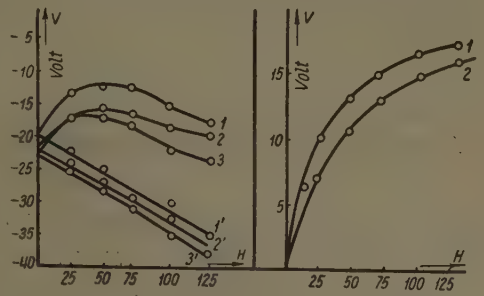

Fig. 2.

Outwardly the effect of a crossed magnetic field becomes apparent in the deviation of the entire discharge toward the wall according to Ampere's law, whereby the direction of the current is given by the drift of electrons in the plasma. Each of the three upper curves (Fig. 2) has a maximum. A weak magnetic field, while it turns the electrons aside from the probe, seems little to affect the heavy mercury ions. On that account the space potential near the probe grows higher. Strong fields, however, extend their influence over the ions and the potential starts decreasing. The probe to which the discharge is pressed becomes negatively charged and is intensively bombarded by positive ions as it may readily be inferred from its sputtering a dust around.

In the case when the mercury vapour contained admixtures the magnetic field was found to bring about the appearance of strata, which drew closer together as the field increased. This is a sequel of the decrease in the mean free path of electrons along the length of the discharge tube.

As the current increases up, the cross potential difference (Hall effect) goes down—this is brought out by the curves in Fig. 2 (right). One of the responsible causes may possibly lie in the pressure increase of mercury vapour due to the increase in current.

Laboratory of Electronic and Ionic Processes.
Physical Institute.
Moscow State University.

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PHYSICS

A METHOD FOR PREPARING NEUTRON SOURCES OF LONG TIME ACTION

By A. POLESSITSKY and A. RATNER

(Communicated by W. G. Khlopin, Member of the Academy, 25.V. 1939)

In order to produce neutrons, the action of α-particles of radioactive elements on beryllium according to the reaction

$$^{9}_{4}\mathrm{Be} + ^{4}_{2}\mathrm{He} \rightarrow ^{12}_{6}\mathrm{C} + ^{1}_{0}n$$

is usually employed. For that purpose ground beryllium is placed in a glass bulb containing radon. The latter, however, decays rather quickly ($T = 3.82$ days), with a simultaneous decrease of the neutron intensity of the source. When there is needed a neutron source of constant intensity during a long time, one has recourse to Ra ($T = 1590$ years) or to RdTh ($T = 1.9$ years) compounds. However, the efficiency of α-particles in these cases is much smaller, for the paths of α-particles in solids are about 20—30 μ, and considerable part of their energy is lost in the radioactive salt itself. To increase the efficiency of α-particles it is necessary to obtain a most intimate mixing of the radioactive atoms with Be. For this purpose we have worked out the following method which gave good results.

A solution of a Ra or RdTh salt was mixed with a neutral solution of $BeCl_2$ (0.8 g $BeCl_2$ in 200 ml H_2O) and with finely ground metallic Be (~2 g). A solution of NH_4OH (containing some Na_2SO_4 in the case of Ra salt) was added, under vigourous stirring, to the mixture. A voluminous colloidal precipitate of Be hydroxide was formed, in which the ground beryllium was uniformly distributed. After 15 min. of stirring, the precipitate was filtered off, carefully dried in a thermostat at 110°, and then ignited in an electric furnace at 300° (to avoid the possibility of inflammation of metallic beryllium) in order to transform Be $(OH)_2$ into BeO. After the ignition, the grey powder of BeO+Be was placed in a golded metallic tube which was carefully soldered to avoid any diffusion of radon or thoron.

A comparison of the intensity of such sources with that of the usual Rn+Be source has shown that in the case of Ra the relative efficiency was equal to 0.8, while in the case of RdTh it was 1.2 (α-particles of RdTh and of its decay products have greater paths and, consequently, a greater power to produce neutrons than those of Ra and of its decay products).

Radium Institute.
Academy of Sciences of the USSR.
Leningrad.

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PHYSICS

IONIZATION IN THE POSITIVE COLUMN

By B. N. KLARFELD

(Communicated by S. I. Wawilow, Member of the Academy, 28.V. 1939)

The number of pairs of ions generated in the positive column may be calculated by using the data on the efficiency of ionization by electron impact, as well as the data on electron concentration and the distribution function of the electron velocities. This quantity may also be obtained experimentally by the probe method (1). It will be greatly interesting to compare these two values, since therefrom it will be possible to establish the connexion between the elementary processes and the complicated ionization phenomena in the discharge. Such a comparison was given in a previous paper (2) which made it possible to determine from the discrepancy between the calculated and experimental data, the character of ionization in the positive column under various discharge conditions. For the efficiency of ionization there had been assumed the following relation:

$$P_i = C_0 p_0 (U - U_0) \text{ with } C_0 = 1.54 \text{ and } U_0 = 12, \quad (1)$$

where P_i is the number of pairs of ions produced per cm of path by an electron of a velocity U volts, and p_0—mercury vapour pressure reduced to 0°C. This relation expresses approximately the values obtained in one of the latest investigations by Smith on the ionization functions (3).

Let it be assumed as previously that α_1 denotes the experimental value of the number of ion pairs generated per electron in the plasma per second, while α_3 is the number calculated by means of equation (1). Then the values for the ratio $\frac{\alpha_1}{\alpha_3}$ show that at the lowest investigated pressure of 0.001 mm Hg, at which direct (non-cumulative) ionization takes place, the value of this ratio is equal nearly to 4.

The non-cumulative ionization under these conditions is confirmed by the constant value of ratio $\frac{\alpha_1}{\alpha_3}$ with the discharge current increasing 100 times, from 0.1 to 10 amperes.

It has been pointed out that the discrepancy between the experimental and calculated values are possibly due to processes similar to the formation of mercury molecule ions by the interaction of excited and normal atoms. This kind of formation of ions was investigated by F. Arnot and I. Milligan (4), who found that it proceeds proportionally to the first power of the discharge current; and therefore the ratio $\frac{\alpha_1}{\alpha_3}$ for the same reason must not change with increasing current. Such an explanation is, however, not sufficiently conclusive, as it implies quite a high efficiency of the process of formation

of the molecule ions. Therefore, it is desirable to examine more in detail the sources causing the discrepancy between α_1 and α_3 under the conditions of non-cumulative ionization in the plasma.

In a recent paper(5) Nottingham has determined anew the shape of the curve of ionization efficiency of mercury atoms. An electrobeam of uniform velocity was obtained by applying a magnetic field. The results of Nottingham in Fig. 1 differ considerably from those of other authors. In the same figure are given similar results obtained by Compton and Van Voorhis (6) and by Smith.

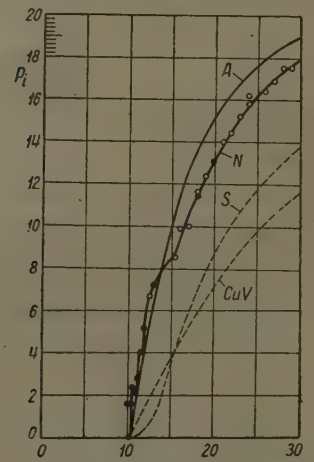

Fig. 1. Number of pairs of ions generated per cm of the path of electron as a function of the electron velocity expressed in volts. C and V—the data by Compton and Van Voorhis, S—data by Smith, N—data by Nottingham, and A—curve by formula (2). The pressure is 1 mm Hg reduced to 0°C.

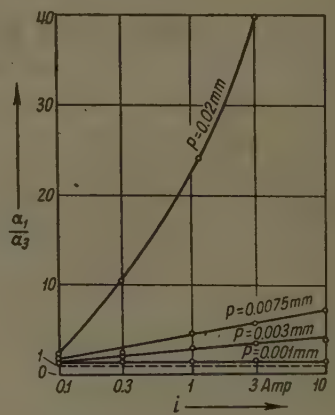

Fig. 2. Ratio $\frac{\alpha_1}{\alpha_3}$ in the positive column of mercury vapour discharge as a function of current and pressure. Diameter of column equal to 32 mm.

In order to use the results obtained by Nottingham in determining the relation between α_1 and α_3 the following approximation of these results has been chosen

$$P_i = A\,[1 - e^{-B\,(U-U_i)}] \text{ with } A = 20 \text{ and } B = 0.15. \qquad (2)$$

The corresponding curve is shown in Fig. 1. For the quantity α_3 we have:

$$\alpha_3 = \int_{c_i}^{\infty} P_i c\, f(c)\, dc, \qquad (3)$$

where c_i is the electron velocity, corresponding to the ionization potential, and $f(c)$ is the distribution function of the electron velocities.

Integration of equation (3) under the Maxwell's distribution of electron velocities results in an expression for α_3 by means of which the ratio $\frac{\alpha_1}{\alpha_3}$ can be calculated already for Nottingham's form of the ionization efficiency curve. This ratio for various values of pressure and current is presented in Fig. 2. Comparison with the corresponding values given in our previous paper shows that with the new form of the ionization efficiency curve the magnitude of $\frac{\alpha_1}{\alpha_3}$ is decreased 3—5 times, although the course of its variation with the pressure and current remains practically unchanged.

Thus, the conclusions, derived in the previous paper, on the non-cumulative character of ionization at 0.001 mm Hg pressure and on the gradual transition to the cumulative form, continue to hold. But the value of the ratio $\frac{\alpha_1}{\alpha_3}$ equal to 4 at 0.001 mm falls to the value of 1.3—1.4, i. e. the calculated value for the number of newly generated ions is lower than the respective experimental value only by 30—40%. And even this discrepancy practically disappears when we take into account that with the considerable drift of electrons taking place at mercury vapour pressures equal to 0.001 mm, the velocity distribution shows a marked distinction from Maxwell's distribution. The relative quantity of fast electrons increases. Using the relation derived by V. Granovsky [see (2)] it may be shown that under the conditions of our experiment the ionization capacity increases owing to this factor by nearly 20%.

Thus, if the measurements by Nottingham are valid, then it can be said that the value of ionization in the low-pressure positive column calculated from the data for the elementary process coincides with the value determined experimentally.

Application of the usual linear approximation expressed by equation (1) to Nottingham's ionization efficiency curve would give a regular deviation from the results calculated by formula (2), this deviation depending upon the value of T_e. However, in cases requiring no great accuracy, it is convenient, in order to simplify calculation, to use equation (1) with the corresponding change of coefficients of C_0 and U_0. Thus, with values of these coefficients equal to $C_0 = 2.15$ and $U_0 = 10.4$, the discrepancy between the results of both approximations with T_e in the range of 12 to 30 000°, as used here, will not exceed 10—15%.

In our previous paper (2) there were presented the solutions of five equations of the plasma, these solutions having been checked for cases of low pressure discharge in helium and mercury vapour. The ionization efficiency curve was used too. The application of Nottingham's data for mercury vapour discharge leads, in this case, to a considerable improvement in the already satisfactory coincidence of the calculated values of the five plasma variables with the results of their experimental check.

And likewise remains completely valid the conclusion of the previous paper that the slope of the straight line giving the effective cross-section for cumulative ionization as a function of the electron energy, is of an order of magnitude higher than that corresponding to non-cumulative ionization. This follows from the fact that under the conditions ($p = 0.0075$ mm and $i = 3$ amperes) applied for calculating the cumulative ionization, the ionization may be considered practically as only cumulative. Indeed, the value of $\frac{\alpha_1}{\alpha_3}$ is now equal to 6 and rapidly increases with increasing current, which is a feature inherent to cumulative ionization.

All-Union Electrotechnical Institute.
Moscow.

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CHEMISTRY

ON THE COMBUSTION OF BOILING EXPLOSIVES

By A. F. BELAJEV

(Communicated by N. N. Semenov, Member of the Academy, 9. V. 1939)

In a previous paper the author has already pointed out the influence of the volatility of an explosive on its decomposition (1). In the present paper the preliminary results of some experiments are described dealing with the combustion of boiling explosives under conditions when the combustion is accompanied by intense convection currents and the evaporation of the latter.

Combustion of Boiling Methyl Nitrate

The main experiments were carried out with methyl nitrate which presents the advantage of an extremely low boiling point. At this low temperature (66°C at atmospheric pressure), no reaction and no additional evolution of heat are observed in the methyl nitrate, and the accumulation of any products which might exert an auto-catalytic effect is excluded.

The combustion of non-boiling methyl nitrate at 20° C proceeds at a rate a little under 1 mm/sec. Strictly speaking, the combustion of the vapour occurs only in the immediate neighbourhood of the surface of the liquid, and the dimensions of the flame are small. In addition to this fundamental flame by which the combustion rate is determined, a bright widely extended «secondary» flame is observed; the latter can be brought in connexion with the oxidation of the burning products of the first flame by the oxygen from the air. If the methyl nitrate is preliminary heated in a small open beaker to 66° C, i. e. to the boiling point, and then ignited by means of a heated wire, the combustion assumes quite a different character. An intense flash is observed followed by a loud popping noise, but the beaker remains undamaged. If the beaker is replaced by a test tube (inner diameter 11—12 mm, 130—150 mm long) and the boiling methyl nitrate be ignited at the bottom, detonation sets in accompanied by a strong disruptive effect (the amount of methyl nitrate was from 0.2 to 0.5 g).

In order to show that the detonation is connected with the boiling process and not with the chemical changes due to the heating of the methyl nitrate to 66°C, the liquid at 20° C was poured into a long, narrow test tube (150 mm long, 7—8 mm inner diameter) connected to a bulb of ca. 1.5 litres capacity which was evacuated by means of an oil pump. When the pressure in the system attained 120 mm Hg, the methyl nitrate began to boil and, upon ignition, it detonated; with the same arrangement, but at 760 mm pressure, the combustion of the ignited methyl nitrate proceeded at a normal rate. We thus see that, in a boiling state, methyl nitrate detonates even if ignited at

20° C (in order to facilitate boiling, some copper filing or bits of glass were placed on the bottom, otherwise boiling proceeded in a very irregular way).

The influence of the boiling process on the development of the detonation is especially clear from the following experiment. Some methyl nitrate heated to 40°C was poured into a test tube which was connected to a bulb of 1.5 litres capacity; the methyl nitrate was ignited, and the system was evacuated. When a definite pressure was attained, the combustion of the methyl nitrate changed to detonation. This must be connected with the process of boiling, since the evacuation causes a decrease of the combustion rate and a more ready removal of the reaction products. Without evacuation, the combustion does not change to detonation. At a temperature of 20° C no detonation is observed. This is probably because the methyl nitrate burns out long before the system is evacuated to the required degree of vacuum.

When the methyl nitrate is heated, considerable evaporation from the surface takes place some time before the liquid begins to boil, though the temperature is close to the boiling point.

The above fact was made use of in the following experiments: some methyl nitrate was poured into a test tube, the lower end of which was immersed in water at 75—80° C. A slightly heated wire was placed in the test tube. At a distance of no more than 30 cm from the surface, the very first vapour formed on the surface of the liquid when it had become warm (at a temperature of some 50—55° C, i. e. in the absence of boiling), was ignited by the wire, and combustion at a normal rate took place. If the wire was placed at a distance of 40—60 mm from the surface, the combustion bore the character of a flash, and finally, if the wire was in the upper part of the test tube outside the warm water, then the first portions of the vapour condensed on the comparatively cool walls of the upper part of the test tube. In the latter case the vapour reaches the wire and can be ignited only when the liquid is heated to 66°C and violent boiling sets in. Upon ignition of the vapour detonation takes place.

The above experiments show in a convincing way that, under the specified conditions, the production of detonation in methyl nitrate (i. e. an accelerated combustion regime causing detonation) is connected with the boiling process and not with the development of the reaction or the chemical changes due to heating.

Combustion of Boiling Nitroglycol (Ethylene Glycol Dinitrate)

The boiling-point of nitroglycol was found equal to 200° C (at 760 mm Hg). When the vapour is removed without further heating, the boiling continues for a long time without any flash, and the thermocouple placed in the boiling nitroglycol shows a comparatively stable temperature of 200 ± 2° C (in these experiments the nitroglycol was contained in a beaker placed on a specially designed electric heater with low inertia). The boiling and the evaporation of the nitroglycol are accompanied by the formation of nitrogen oxides indicating that at this temperature the nitroglycol is decomposed to a considerable extent. However, it can be shown that, even under the given conditions, when the liquid is considerably heated and a violent reaction proceeds, the nature of the chemical decomposition produced by ignition is different according as boiling does or does not take place. Thus, when the nitroglycol was heated in a beaker the wire being placed at some 15—20 cm from the surface (as in the case of methyl nitrate), the ignition occurred at 185—188° C (the temperature being read on a thermocouple immersed in the nitroglycol), i. e. at the moment when as yet there is no boiling, but a strong evaporation

takes place from the surface. The latter circumstance, which permits to ignite the nitroglycol under such conditions when the slightest increase of temperature would cause a violent boiling, allowed us to measure the combustion rate of nitroglycol at temperatures just below that at which the flash is usually observed. At 185° C the combustion rate of the nitroglycol was found equal to 0.65 mm/sec., i. e. a little more than the double of that measured at 20° C. If nitroglycol is ignited under similar conditions (200° C), then, just as in the case of boiling methyl ether, a violent flash is observed accompanied by a loud popping noise. But if the nitroglycol boils on the bottom of the test tube, the ignition produces detonation.

An accelerated combustion of nitroglycol can also be observed at temperatures lower than 200° C. As in the case of methyl nitrate it will suffice for this purpose to reduce the pressure and thus to lower the boiling point of nitroglycol.

A close analogy between methyl nitrate and nitroglycol has thus been established; in spite of the high boiling point of nitroglycol, here just as in the case of methyl nitrate, the presence or absence of boiling alters the nature of the explosive decomposition produced by ignition in a very pronounced way.

To sum up the description of the experimental results obtained, it must be noted that in the majority of cases the detonation was complete (as a rule, in the presence of violent boiling) with a strong action on the support; however, sometimes the detonation was not complete, the test tube burst into pieces, but the action on the foundation was insignificant.

Discussion of the Results

In the case of boiling explosives, the mechanism of the transition from combustion to detonation can be outlined as follows. During the boiling, a violent splashing of the explosive takes place, «injection» of the latter into the combustion zone and a thorough agitation of the liquid. The combustion in parallel layers is thus disturbed, the evaporation accelerates, as well as the combustion. The general character of the combustion which is accompanied by a rather loud popping noise leads us to the conclusion that the combustion rate during boiling is at least a hundred times greater than it is in the absence of boiling. It is this considerable acceleration of the combustion which is the main factor characterizing the combustion of boiling nitroglycol and methyl nitrate. The development of detonation upon boiling appears to be a secondary effect, due to the more difficult removal of the products of this accelerated combustion which may quickly lead to a local increase in pressure. This might facilitate the development of detonation in the vapour and its passing over to the condensed phase.

The stable combustion of colloidal propellants without any detonation might partly be explained by the fact that in the case of a colloidal structure boiling takes place on the surface only, the violent boiling of considerable masses accompanied by a thourough agitation of the substance being excluded, so that the combustion in parallel layers becomes more stable.

Institute of Chemical Physics.
Leningrad.

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CHEMISTRY

SYNTHESIS OF SOME MONOSUBSTITUTED HOMOLOGUES OF CYCLOPENTANE HAVING A NORMAL SIDE-CHAIN

By A. F. PLATE

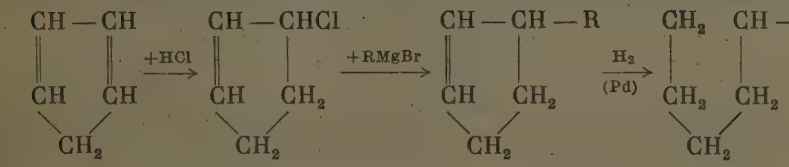
(Communicated by N. D. Zelinsky, Member of the Academy, 19. V. 1939)

The synthesis of cyclopentane homologues is of interest as some crude oils, Baku crude oils from USSR particularly, contain considerable amounts of hydrocarbons of the cyclopentane series. Besides, they are interesting because, as it has been shown by Zelinsky, Kasansky and Plate (1), cyclopentane and its homologues in the presence of hydrogen and of a platinum catalyst undergo, at a temperature of 305—310°, a rupture of the five-membered ring with the formation of paraffinic hydrocarbons having mainly a branched structure. Simultaneously a partial conversion into aromatic hydrocarbons takes place, too (2). Up to now only a few and besides the most simple representatives of this series have been synthetized. The main method for the preparation of monosubstituted cyclopentane homologues is the action of cyclopentanone upon the corresponding alkyl-magnesium haloid and the subsequent dehydration of the tertiary alcohols to unsaturated hydrocarbons which are then hydrogenated. Secondary alkyl-cyclopentanes which ordinarily cannot be synthetized according to the method described above, are easily obtained by way of the hydrogenation of the corresponding fulvenes (3).

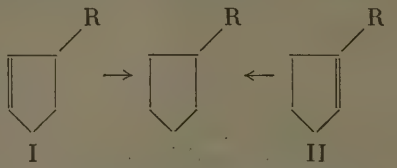
Among the monosubstituted cyclopentane homologues having a normal side-chain the following hydrocarbons have been synthetized up to now: methyl-(4), ethyl-(5), *n*-propyl-(5), *n*-butyl-(5), *n*-hexyl (6) and *n*-octyl-cyclopentanes (6). In the present paper the preparation of n-amyl- and *n*-heptyl-cyclopentanes is described, as well as the preparation of the intermediate products—the corresponding tertiary alcohols and cycloolefins.

Besides, the synthesis of *n*-hexyl-cyclopentane has been repeated, because Zelinsky, Mikhlina and Eventova (6) who were the first to obtain it, had dealt with a small amount of the substance, of the order of 6—7 g, and this had made it difficult to submit the product to a careful fractional distillation.

Along with the ordinary way through cyclopentane and a tertiary alcohol we have also tried another method for the synthesis of cyclopentane homologues using cyclopentadiene as the initial substance. By means of this method, v. Braun, Kamp and Kopp (7) have synthetized Δ^2- substituted cyclopentenes, ethyl-cyclopentene-2 with a 30 p. c. yield and isoamyl cyclopentene-2 with a 60 p. c. yield. This synthesis can be expressed by the following scheme:



Cyclopentenyl chloride which can be obtained with a good yield (about 85 p. c.) may be considered as a cyclic homologue of allyl chloride and, like the latter, it reacts readily with alkyl-magnesium haloids. By using this method we synthetized *n*-amyl-cyclopentene-2 and *n*-hexyl-cyclopentene-2, through the hydrogenation of which the same saturated hydrocarbons were obtained as by the method when cyclopentanone was being used as the initial product:



I II

It should be pointed out that the compounds of type I, i. e. Δ^2-substituted cyclopentenes, have a lower boiling point and smaller specific gravity and refractive index compared with compounds of type II, i. e. Δ^1-substituted. This method may prove as well to be usefull for the synthesis of other cyclopentane homologues and we propose to investigate this.

The compounds of type I, judging from the method of their synthesis, are entirely individual substances, whereas the compounds of type II may often contain as an admixture a small amount of isomerides having a semi-cyclic double bond, which may be formed also through the dehydration of tertiary alcohols.

Experimental

n-Amyl-Cyclopentanol-1

n-Amyl alcohol was prepared by the Grignard method from propyl-magnesium bromide and ethylene oxide using the procedure given for *n*-hexyl alcohol ([8]). *n*-Amyl bromide, as well as all the other bromides mentioned below, was prepared as usual by means of the HBr and H_2SO_4 method ([9]). *n*-Amyl-cyclopentanol-1 was prepared by the Grignard reaction from *n*-amyl magnesium bromide and cyclopentanone. $1^1/_2$ moles of all the reagents were used. After fractionating it three times in vacuo, pure *n*-amyl-cyclopentanol-1 was isolated with a 42.5 p. c. yield:

b. p. 85—87°/7 mm; n_4^{20} 1.4530; d_4^{20} 0.8957.

Found: MR_D 47.58; MR_D 47.70 calculated for $C_{10}H_{20}O$.

In a recent paper by Rinkes([10]) the author gives only the b. p. 101—103°/10 mm for this alcohol.

n-Amyl-cyclopentene-1

The dehydration of *n*-amyl-cyclopentanol was carried out by means of a 20 p. c. aqueous solution of oxylic acid. Yield 70—80 p. c.:

b. p. 177—179°/743 mm; n_D^{20} 1.4513; d_4^{20} 0.8108.

Found: MR_D 45.89; MR_D : 45.71 calculated for $C_{10}H_{18}$ with F

Rinkes ([10]) gives only the b. p. 178—180°.

n-Amyl-cyclopentene-2*

n-Amyl-cyclopentene-2 was obtained from *n*-amyl magnesium bromide and cyclopentenyl chloride([7]). Yield 43 p. c.

b. p. 173.5—175.2°/747 mm; n_{D}^{20} 1.4455; d_4^{20} 0.8022.

Found: MR_D 45.87; MR_D calculated for $C_{10}H_{18}$ with F: 45.71.

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* O. D. Sterligov of the Chemical Faculty at the State University of Moscow, has participated in the synthesis of this hydrocarbon and in its subsequent hydrogenation.

Anal. subs. 4.041 mg; CO_2 12.917 mg; H_2O 4.791 mg.
Subs. 4.914 mg; CO_2 15.726 mg; H_2O 5.723 mg.
Found %: C 87.11, 87.28; H 13.27; 13.03.

Calcd. for $C_{10}H_{18}$ %: C 86.87; H 13.13*.

n-Amyl-cyclopentane

n-Amyl-cyclopentane was obtained through the hydrogenation of *n*-amyl-cyclopentene-1 in the presence of Pd-black in an alcohol solution in the cold:

b. p. 178—179°/752 mm; n_D^{20} 1.4356; d_4^{20} 0.7898.
Found: MR_D 46.36; MR_D calculated for $C_{10}H_{20}$:46.18.

Anal. subs. 4.110 mg; CO_2 12.930 mg, H_2O 5.230 mg.
Subs. 3.016 mg; CO_2 9.500 mg; H_2O 3.905 mg.
Found %: C 85.80; 85.91; H 14.24,14.45.

Calcd. for C_nH_{2n} %: C 85.62; H 14.38.

The same hydrocarbon was obtained through the hybrogenation of *n*-amyl-cyclopentene-2:

b. p. 178.4 — 179.6°/748 mm; n_D^{20} 1.4359; d_4^{20} 0.7893.
Found: MR_D 46.42; MR_D calculated for $C_{10}H_{20}$: 46.18.

n-Hexyl-cyclopentanol-1

n-Hexyl-cyclopentanol-1 was obtained by the Grignard reaction from cyclopentanone and *n*-hexyl magnesium bromide([6]) (the *n*-hexyl alcohol from Kahlbaum was used). In order to minimize the reactions of the condensation of cyclopentanone as well as of the dehydration of *n*-hexyl-cyclopentanone, an excess of the Grignard reagent compared to the cyclopentanone was used (1 $^1/_4$: 1 mole) and after the addition of the cyclopentanone the reaction mixture was not heated. The yield of *n*-hexyl-cyclopentanol-1 after three consecutive distillations in vacuo was 84 g (50 p. c. of the theoretical). In those runs when the reagents were taken in equimolecular proportions and when the reaction mixture was heated for 1 hour on a water bath after the addition of the cyclopentanone, the formation of a considerable amount of a high boiling residue, as well as of a lower boiling fraction containing *n*-hexyl-cyclopentene, was always observed. The yield of *n*-hexyl-cyclopentanol-1 (2 moles of the initial reagents were used) was in this case only 21 p. c. and the product obtained had higher physical constants, which were near to the constants of *n*-hexyl-cyclopentanol given in the paper mentioned above([6]).

The physical constants of pure *n*-hexyl-cyclopentanol-1 isolated by us were as follows:

b. p. 85—86°/4 mm; n_D^{20} 1.4600; d_4^{20} 0.8921.
Found: MR_D 52.37; MR_D calculated for $C_{11}H_{22}O$: 52.32.

Anal. subs. 0.1240 g; CO_2 0.3520; H_2O 0.1442 g.
Subs. 0.1004 g; CO_2 0.2844 g; H_2O 0.1147 g.
Found %: C 77.42, 77.26; H 13.01, 12.78.

Calcd. for $C_{11}H_{22}$ %: C 77.57; H 13·03.

n-Hexyl-cyclopentene-1

n-Hexyl-cyclopentene-1 was prepared through the dehydration of *n*-hexyl-cyclopentanol-1 by means of a 20 p. c. aqueous solution of oxalic acid. Yield 72 p. c.:

b. p.202—204.5°/743 mm; n_D^{20} 1.4540; d_4^{20} 0.81.58
Found: MR_D 50.51; MR_D calculated for $C_{11}H_{26}$ with F: 50.33.

Anal. subs. 4.418 mg;CO_2 14.015 mg; H_2O 5.357 mg.
Subs. 4.204 mg; CO_2 13.345 mg; H_2O 5.031 mg.
Found %: C 86.51, 86.57; H 13.57, 13.39.

Calcd. for $C_{11}H_{20}$%: C 86.75, H 13.25

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* The analysis was carried out in the microanalytical laboratory of our Institute by M. O. Korshun and S. Th. Kalugina.

From the fraction 200—220° (the lowest boiling fraction obtained in the synthesis of *n*- hexyl-cyclopentanol-1) after its dehydration with an aqueous solution of oxalic acid and reflexing over sodium, the following fractions were isolated:

Fraction 203—206°/747 mm; n_D^{20} 1.4476; d_4^{20} 0.8008.
Found: MR_D 50.83; MR_D calculated for $C_{11}H_{20}$ with F: 50.33.
Fraction 206—210°/747 mm; n_D^{20} 1.4415; d_4^{20} 0.7902.
Found MR_D 50.91; MR_D calculated for $C_{11}H_{20}$ with 50.33.

During the distillation of these fractions it was found that the refractive index and the specific weight decreased with the increase of the temperature. This probably showed the presence of an admixture of a paraffine hydrocarbon (dodecane) that had a higher boiling point and lower refractive index and specific gravity. In order to prove the presence of dodecane, the fraction 206—210° was repeatedly treated with concentrated sulphuric acid, the hydrocarbon residue washed with sodium carbonate, dried over calcium chloride and distilled over metallic sodium. The physical constants of the hydrocarbon obtained are near to those of dodecane:

b. p. 213—215°/763 mm; n_D^{20} 1.4245; d_4^{20} 0.7562.
Found MR_D 57.48; MR_D calculated for $C_{12}H_{26}$ 57.62.

[Data found in the literature for dodecane ([11]):
b. p. 215°; n_D^{20} 1.4217; d_4^{20} 0.7495].

It seems very probable that the specific gravity and the index of refraction of *n*-hexyl-cyclopentene-1 given in the above mentioned paper([6]) (n_D^{20} 1.4490; d_4^{20} 0.8079) were lower than the constants for this hydrocarbon found in the present paper due to an admixture of dodecane.

n-Hexyl-cyclopentene-2

This hydrocarbon was obtained in the same way as *n*-amyl-cyclopentene-2. We used 0.3 mole of the initial reagents. Yield, 38 p. c.

b. p. 196.8—198.8°/761 mm; n_D^{20} 1. 4480; d_4^{20} 0.8067.
Found: MR_D 50.50; MR_D calculated for $C_{11}H_{20}$ with F: 50.33

Anal. subs. 4.646 mg; CO_2 14.785 mg; H_2O 5.405 mg.
Subs. 4.528 mg; CO_2 14.375; H_2O 5.424 mg.
Found %: C 86.79, 86.64; H 13.02, 13.41.
Calcd, $C_{11}H_{20}$ %: C 86.75, H 13.25.

n-Hexyl-cyclopentane

n-Hexyl-cyclopentane was obtained through the hydrogenation of *n*-hexyl-cyclopentene-1 with Pd-black in the cold:

b. p. 201.1—202.2°/742 mm; n_D^{20} 1.4394; d_4^{20} 0.7597.
Found MR_D 51.01; MR_D calculated for $C_{11}H_{20}$: 50. 80.

Anal. subs. 5.061 mg; CO_2 15.917 mg; H_2O 6.504 mg.
Subs. 4.710 mg; CO_2 14.771 mg; H_2O 6.068 mg.
Found % : C 85.77; 85.59; H 14.38, 14.42.
Calcd. for C_nH_{2n}% : C 85.62; H 14.38.

The same hydrocarbon was obtained through the hydrogenation of *n*-hexyl-cyclopentene-2:

b. p. 200.8 — 202°/745 mm; n_D^{20} 1.4392; d_4^{20} 0.7956.
Found MR_D 50.99; MR_D calculated for $C_{11}H_{22}$: 50.80

n-Heptyl-cyclopentanol-1

This alcohol was obtained by the Grignard reaction from cyclopentanone *n*-heptyl-magnesium bromide (the *n*-heptyl alcohol from Kahlbaum was

used). 2 moles of the reagents were taken. Yield, 50 p. c. This alcohol is readily dehydrated making it difficult to isolate it in a pure state:

b. p. 91—92°/3 mm; n_D^{20} 1.4604; d_4^{20} 0.8817.

When cooled to a temperature lower than—18° crystals begin to form.
Found: MR_D 27.26; MR_D calculated for $C_{12}H_{24}$: 56.94.

Anal. subs. 0.1301 g; CO_2 0.3744 g; H_2O 0.1678 g.
Subs. 0.0899 g; CO_2 0.2579 g; H_2O 0.1100 g.
Found %— C 78.49, 78.24; H 13.57, 13.69.

Calcd. for $C_{12}H_{24}$%: C 78.18; H 13.13.

n-Heptyl-cyclopentene-1

n-Heptyl-cyclopentene-1 was obtained through the dehydration of *n*-heptyl-cyclopentanol-1 with a small crystal of iodine ([12]). Yield, 48 p. c.:

b. p. 218—220°/762 mm; n_D^{20} 1.4555; d_4^{20} 0.8176.

Found: MR_D 55.20; MR_D calculated for $C_{12}H_{22}$ with F: 54.95

Anal. subs. 3.778 mg; CO_2 11.990 mg; H_2O 4.506 mg.
Subs. 6.522 mg; CO_2 20.721 mg; H_2O 7.600 mg.
Found %: C 86.55, 86.64; H 13.36, 13.04.
Calcd. for $C_{12}H_{22}$ %: C 86.65; H 13.35.

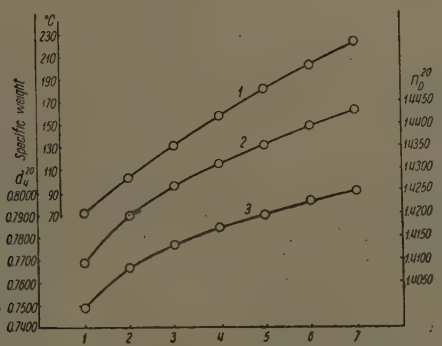
n-Heptyl-cyclopentane

n-Heptyl-cyclopentane was obtained through the hydrogenation of *n*-heptyl-cyclopentane-1 with Pd-black at room temperature:

b. p. 222.1 — 224°/741; mm; n_D^{25} 1.4430; d_4^{20} 0.8002.

Found: MR_D 55.73; MR_D calculated for $C_{12}H_{22}$: 55.42.

Anal. subs. 0.0640 g; CO_2 0.2007 g; H_2O 0.0802 g.
Subs. 0.0696 g; CO_2 0.183 g; H_2O 0.0875.
Found %: C 85.53, 85.54; H 14.02, 14.04.
Calcd. for C_nH_{2n}%: C 85.62; H 14.38.



Curves of the change of physical constants of substituted cyclopentane homologues having an unbranched side-chain. Boiling point *1*; refractive index *2*; specific weight *3*.

The physical constants of all the compounds obtained are given in the following table. In Fig. 1 the curves are given showing the changes of the physical constants of monosubstituted cyclopentane homologues having an unbranched side-chain containing from one to seven carbon atoms.

	Boiling point		n_D^{20}	d_4^{20}	MR_D	
	°C	mm			found	calcd.
n-amyl-cyclopentanol-1	85—87	7	1.4530	0.8957	47.57	47.70
n-hexyl-cyclopentanol-1	85—86	4	1.4600	0.8921	52.37	52.38
n-heptyl-cyclopentanol-1	91—92	3	1.4604	0.8317	57.26	56.94
n-amyl-cyclopentene-1	177—179	743	1.4513	0.8128	45.89	45.71
n-hexyl-cyclopentene-1	202.204.5	743	1.4540	0.8158	50.51	50.33
n-heptyl-cyclopentene-1	218—220	762	1.4555	0.8176	55.20	54.95
n-amyl-cyclopentene-2	173.5—175.2	747	1.4455	0.8022	45.87	45.71
n-hexyl-cyclopentene-2	196.8—198.8	761	1.4480	0.8067	50.60	50.33
n-amyl-cyclopentane	178—179	752	1.4356	0.7898	46.36	46.18
n-hexyl-cyclopentane	201.1—202.2	742	1.4394	0.7957	51.01	50.80
n-heptyl-cyclopentane	221.1—224	751	1.4430	0.8002	55.75	55.42

Conclusions

1. The following compounds have been synthetized: *n*-amyl-, *n*-hexyl and *n*-heptyl-cyclopentanol-1, *n*-amyl-, *n*-hexyl- and *n*-heptyl-cyclopentene-1, *n*-amyl- and *n*-hexyl-cyclopentene-2, *n*-amyl, *n*-hexyl- and *n*-heptyl-cyclopentanes.

2. It has been demonstrated that Δ^2-substituted cyclopentenes have lower constants (b. p., refractive index, specific gravity) than the corresponding Δ^1-substituted cyclopentenes.

3. A method for the preparation of monosubstituted cyclopentane homologues, using cyclopentadiene as the initial product and obtaining Δ^2-substituted cyclopentenes as intermediates, has been proposed.

Department of N. D. Zelinsky, Member of the Academy.
Institute of Organic Chemistry.
Academy of Sciences of the USSR.

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CHEMISTRY

USE OF THE KURNAKOV RECORDING PYROMETER IN THE STUDY OF CHANGES IN STARCH

By V. NAZAROV and A. NIKOLAEV

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In the preceding paper (1) it was shown that when studying starch gelatinization, an objective method for the examination (of heating curves) can be used. The experiments described in the paper have been continued and amplified. In general no fundamental changes have been introduced in the method of operation. We have succeeded only in getting clear thermograms, the time of test being shortened. If the heating curves are produced under the same conditions (quantity of water, starch, rate of heating) the stop of gelatinization recurs.

The rate of heat as well as the change in concentration have but a small effect upon the results obtained. The difference in the gelatinization temperatures observed in the study varied within one degree C (from 60.8 to 61.8°C).

With very weak concentrations of the initial suspensions it was difficult to record the stop in the ordinary way because of the thermal effect of gelatinization being small, as expressed in absolute units.

If, however, a differential record is resorted to, the endothermal effect becomes apparent.

The gelatinization temperature of the given samples of starch determined according to S. V. Gorbachev's method was 61.75° C. In all of the tests a pronounced endothermal effect was observed.

In the work of Rodewald (2) there were some indications of the heat absorption during the swelling of starch. Kruyt (3) and his associates by means of thermal measurements observed a certain decrease in temperature during the process of gelatinization. But this problem, very interesting, indeed, from the stand-point of both practice and theory, has not been treated further in the above-mentioned works. After our first report had already been published in the C. R. Acad. Sci. URSS in 1938, there appeared in the January issue of Kolloid Zeitschrift 1939 an article by A. Küntzel and K. Doener (4) devoted to the problem of starch gelatinization. One of their papers described a method similar to ours, but the differential record alone was made use of by these authors. They also observed the endothermal effect of starch gelatinization. But while using the method they did not study the influence of electrolytes on the process of gelatinization.

The heating curves obtained by us for potato starch suspensions in the 1/1 *N* solutions of sodium chloride, potassium chloride and potassium nitrate,

show the stops to lie at the temperatures which are in good agreement with the results obtained by using a different method.

1/1 *N* solutions	NaCl	KCl	KNO_3
	$t°$	$t°$	$t°$
According to Gorbachev's method	67.70	58.8	57.1
From our heating curves	62.50	57.5	56

Thus, our interpretation of the stop in the gelatinization of starch as a result of a very sharp alteration in the thermal conductivity on the formation of jelly has received further confirmation.

We continued our investigation by immersing the differential thermocouple into freshly made and cooled starch jelly instead of water. Here again an endothermal process was noticed by means of the differential record. Thus, the endothermal effect at the gelatinization of starch has been proved experimentally (Fig. 1).

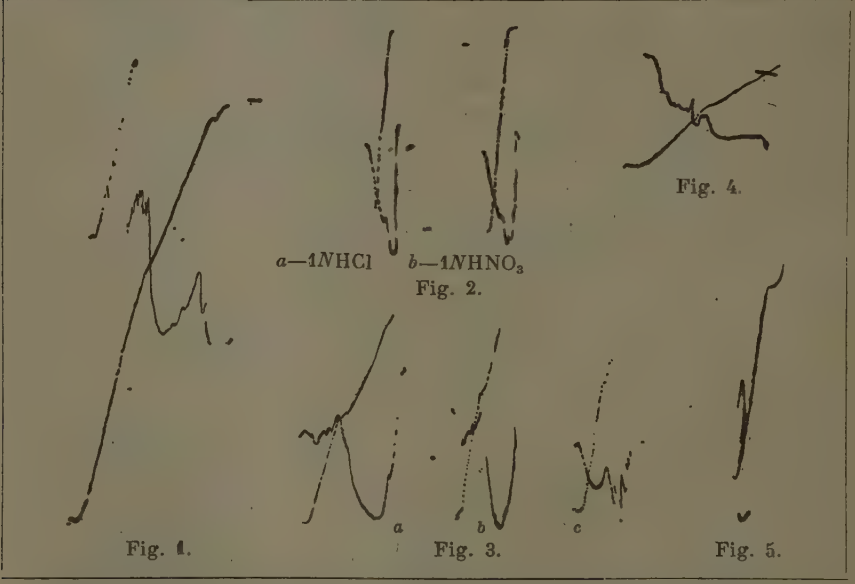

Fig. 1. Fig. 2. Fig. 3. Fig. 4. Fig. 5.

When heating the suspensions of starch in a 1/1 *N* solution of chloric acid and nitric acid we obtained the following result: first, at a certain temperature the gelatinization of starch with the formation of jelly takes place. The jelly gets clarified from the periphery to the centre which is followed by the process of its dissolution. Here the process of gelatinization is followed by the process of dextrinization. When the corresponding thermograms (Fig. 2) are examined, the curves of the differential record show that the endothermal stop of gelatinization is followed by the endothermal stop of dextrinization.

The first stop is related to the disintegration of starch granules which results in the break of bonds between the groups of micellas and individual micellas. Further disintegration into separate micellas requires some more

energy which is illustrated on the differential record by the stop of dextrinization and the still more pronounced endothermicity. In this connexion it is worth while to examine the thermograms for the starch treated during several days with the 2*N* solution of chloric acid. In Fig. 3 are given the curves for the starch treated with the acid solution during 2 and 7 days respectively (*b* and *c*).

By way of comparison we shall refer to the heating curve for an ordinary soluble commercial starch. One of the methods of getting soluble starch is to treat it with some acids. The heating curve (Fig. 3,*b*) for the starch heated during two days with acid is similar to that obtained in the heating of commercial soluble starch (Fig. 3,*a*). The thermograms show that the starch treated with the acid solution during one week undergoes in the cold a partial dextrinization.

It is interesting to note that if in the first days of the digestion of starch with acid the temperature of gelatinization goes down, it goes up further on in such a way that at last the level is obtained which exceeds the temperature of the native starch gelatinization. We have also the heating curve for the suspension of starch in formamid which is also a starch solvent. In that case the stop of gelatinization was observed at much lower temperatures than those for water starch suspensions (51.5° C), the general character of the curve being the same (Fig. 4).

In the conclusion of our short report we shall give the heating curve for air-dried starch (Fig. 5).

It is quite obvious that water is lost by the starch within a certain range of temperature. The phenomenon shows quite clearly that the granules of starch lose water in a process of a polythermal character. There is no doubt that it is connected with the different character of water bounds in starch ([5]). The heating curves for dry starch and similar products (flour, etc.) are of very great practical importance as they make it possible to determine the range of temperature required for drying the corresponding products, while making the analytical determinations of moisture.

Institute of General and Inorganic Chemistry.
Academy of Sciences of the USSR.
Moscow Institute of Bread and Candy Industry.

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CHEMIE

ZUSAMMENWIRKUNG VON KASEIN MIT WASSERLÖSUNGEN VON ANILIN UND PIRIDIN

Von A. J. KOROLEW und B. A. WILENSKI

(Vorgelegt von N. D. Zelinsky, Mitglied der Akademie, d. 10. V. 1939)

In der ersten Mitteilung zeigten wir, dass die Bindung schwacher organischer Säuren durch Kasein aus Wasserlösungen einen doppelten Charakter hat: erstens bilden sich Proteinsalze, zweitens geht die Sorption undissoziierter Moleküle der organischen Säure durch Eiweiss vor sich. Diese Bildungsart wurde früher nicht beachtet.

Die vorliegende Untersuchung setzte sich zum Ziel, von demselben Standpunkt aus das Zusammenwirken von Eiweisstoffen mit einigen schwachen organischen Basen in Wasserlösungen zu untersuchen. Als Untersuchungsobjekt wählten wir Anilin und Piridin. Da uns eine geeignete Elektrode für die Aktivitätenmessungen der $H^{\pm}$-Ione in Lösungen von Piridin und Anilin fehlte, mussten wir auf die in der vorhergehenden Mitteilung erwähnten potentiometrischen Messungen verzichten. Hier waren wir gezwungen uns auf die vergleichende Untersuchung der Bindung von organischen Basen in Kaseinsolen und Kalium-Kaseinat zu beschränken, was auch die Abgrenzung zweier verschiedenen Arten der Bindung organischer Basen durch Eiweisstoffe ermöglichte.

In der Literatur sind Angaben über die Zusammenwirkung organischer Basen mit Eiweisstoffen vorhanden.

Die stimulierende Wirkung von Harnstoff, Piridin und einiger anderer Stoffe auf die Quellung der Gelatine war ausser von Chiari (1) (s. I. Mitteilung) auch von M. Fischer (2) festgestellt worden, der zeigte, dass die Wirkung dieser Stoffe nur teilweise durch deren Laugenfunktion erklärt werden kann. In seinem Artikel weist der Verfasser auf irgendeine andere Funktion der untersuchten organischen Basen hin, die die Quellung der Eiweisstoffe bedeutend erhöht und bei einer gewissen Konzentration diese in gelösten Zustand überführt.

Diese Tatsachen lassen eine molekulare Sorption derartiger organischer Stoffe durch Eiweiss vermuten. Der experimentelle Nachweis einer solchen Bindung wurde in 1927 von K. Meyer (3) erbracht, der die Sorption von 0-Nitranilin durch Kasein und andere Eiweisstoffe feststellte. Die Bindung von Anilin und Phenol durch Kasein wurde in der vorher erwähnten Arbeit von Wilenski und Pawlowa festgestellt.

Aus der angegebenen Literatur ist ersichtlich, dass die Proteine fähig sind mit einigen organischen Basen zusammenzuwirken, wobei diese Zusammenwirkung mit der Quellung oder dem Auflösen der Eiweisstoffe verbunden ist. Auf Grund dieser Angaben war es von Interesse, die Zusammenwirkung

von Eiweisstoffen mit Anilin und Piridin eingehender zu untersuchen und zu prüfen, ob nicht ausser der gewöhnlichen chemischen Bindung schwacher Basen, auch eine Sorption der undissoziierten Moleküle von Anilin und Piridin vor sich geht, die mit der Quellung und dem Auflösen der Proteine, d. h. der Solvatation der Eiweisstoffe, durch diese organischen Stoffe verbunden ist.

Wie auch in der vorhergehenden Mitteilung, wurde die Verteilung des organischen Stoffes auf beiden Seiten der Membran bei der Gleichgewichtsdialyse der Eiweissole untersucht. Die Kollodium-Membranen wurden in diesem Falle denitriert infolge der chemischen Zusammenwirkung des Membranstoffes mit Anilin und Piridin. Die Denitrierung der Membranen wurde in einer alkoholischen Lösung $(NH_4)_2S$ eine Stunde lang vorgenommen, wonach die Zellen sorgfältig mit Wasser gewaschen wurden. Die Bindung organischer Basen durch Kasein Γ wurde aus der mit einem Interferometer bestimmten Konzentrationsänderung des organischen Stoffes in der äusseren Flüssigkeit ΔC berechnet. Ist g die Konzentration von Kasein in g/l, so ist

$$\Gamma = \frac{\Delta C(V_1 + V_2)}{gV_2}$$

wo V_1—das Volumen der zum Auflösen des Eiweisstoffes verwendeten Flüssigkeit und V_2—dasjenige der äusseren Flüssigkeit ist.

Die Kalium-Kaseinatsole bereitete man durch Auflösen von Kasein in einer 0.09 N Lösung von KOH vor, der eine geringe Menge von Natrium-Hydrosulfit (1.4 g auf einen Liter Lösung) hinzugefügt wurde, um die Bildung von gefärbten Stoffen der Anilinoxydation zu verhindern. Für die interferometrischen Messungen war es erforderlich, sich von den in der äusseren Flüssigkeit und in der Ausgangslösung vorhandenen Elektrolyten zu befreien (KOH und $Na_2S_2O_4$). Zu diesem Zweck wurden beide Flüssigkeiten in einem geschlossenen Glasgerät destilliert. Die äussere Flüssigkeit wurde nur in solchen Fällen destilliert, wenn sie keine merklichen Mengen des von innen diffundierten Eiweisses enthielt.

In der Tabelle 1 sind Angaben über die Bindung bei verschiedenen Konzentrationen von Anilin und Kasein wiedergegeben.

Tabelle 1

C-Konzentration der organischen Base in mol/l

ΔC	g	Γ, mol/g · 10^3
0.22	10	0.64
0.33	10	1.07
0.11	30	0.19
0.22	30	0.55
0.33	30	1.17
0.11	40	0.17
0.22	40	0.52
0.33	40	1.11
0.11	60	0.17
0.22	60	0.51
0.33	60	1.00

In allen von uns untersuchten Fällen ging im Dialyseprozess eine Verringerung der Anilinkonzentration in der äusseren Flüssigkeit vor sich, was sich durch die Bindung von $C_6H_5NH_2$ durch Eiweiss erklärt. Das Anilin ging aus der äusseren Flüssigkeit in das Sol solange über, bis die Anilinkonzentration auf beiden Membranseiten gleich wurde. Die Gleichheit der Anilinkonzentrationen in beiden Flüssigkeiten nach Dialysenabschluss scheint der Wahrheit ausserordentlich nahezustehen, da in Anwesenheit von KOH die Anilinbetei-

ligung bei der Salzbildung «Anilin-Kaseinat» ausserordentlich gering ist; die Berichtigung für die Anilinbeteiligung in dem Donnanschen Gleichgewicht kann nicht bedeutend sein, denn in einem stark basischen Milieu geht fast keine elektrolytische Anilindissoziation vor sich.

Die Anilinsorption durch Kalium-Kaseinat stellt eine Bindung von undissoziierten Anilinmolekülen durch Eiweiss dar. Für diese Behauptung spricht die Tatsache, dass das Anilin als sehr schwache Base nicht fähig ist, sich in Anwesenheit von KOH an der Eiweissalzbildung zu beteiligen. Die von uns festgestellte Sorption betrachten wir als Resultat einer solvatationsartigen Anilinbindung durch Kasein, was sich durch die Fähigkeit des Kaseins in reinem Anilin zu quellen, d. h. sich dem Solvatationsprozess durch diese Flüssigkeit zu unterziehen, bestätigt.

Es war von Interesse, die Gesetzmässigkeit bei der Solendialyse von Kalium-Kaseinat zu prüfen und an einer anderen organischen Base zu bestätigen. Zu diesem Zweck wählten wir Piridin. Dieser Stoff war deswegen noch von grossem Interesse, weil er eine starke lösende Wirkung bezüglich Kasein, Gelatine und anderer Eiweisstoffe in wässrigen Lösungen besitzt. Da es möglich war Kaseinsole in Piridinlösungen in grösserem Konzentrationsbereich des Piridin in Wasser zu erhalten, konnte die Piridinbindung nicht nur durch Kalium-Kaseinat, sondern auch durch Kasein untersucht werden. Diese Versuche sollten auch das Bestehen zweier Arten von Piridinbindung durch Kasein zeigen: einer chemischen Bindung und einer Eiweissolvatation durch organischen Stoff. Bei der Aufstellung von zwei Versuchsreihen mit Kalium-Kaseinat und Kasein war es zu erwarten, dass beim Fehlen von KOH die Piridinaufnahme durch Eiweiss grösser als in KOH enthaltenden Lösungen sein wird, da im ersten Falle ausser der Sorption der Piridin-Moleküle das Kasein als Säure reagiert, indem es Salz bildet. Die Ergebnisse der Versuche mit der Solendialyse von Kalium-Kaseinat und Kasein sind in Tabelle 2 dargestellt. Die Untersuchung der Sorptionserscheinungen in Kaseinsolen war in grossem Konzentrationsbereich des Piridins (0.248—8.06 mol/l) vorgenommen.

Die Piridinverteilung bei der Solendialyse von Kalium-Kaseinat wurde in kleinerem Abschnitt der Piridinkonzentrationen (bis 1.24 m/l) untersucht.

In dem untersuchten Gebiet der Piridinkonzentrationen für die Sole von Kasein und Kalium-Kaseinat (0.248—1.240 m/l) wurde eine Verringerung der Piridinkonzentration in der äusseren Flüssigkeit, d. h. Piridinbindung durch das Eiweiss, beobachtet. Aus den experimentellen Angaben folgt,

Tabelle 2

C, mol/l	Kalium-Kaseinat		Kasein	
	g	Γ, mol/g · 10^3	g	Γ, mol/g · 10^3
0.248	60	0.21	57.3	0.32
0.496	60	0.33	57.3	0.63
0.744	60	0.60	57.3	0.95
0.992	—	—	57.3	1.19
1.240	60	1.18	57.3	1.47
2.08	—	—	57.3	1.98
2.48	—	—	57.3	1.92
3.72	—	—	57.3	0.56
3.97	—	—	57.3	0.48
4.34	—	—	57.3	0.0
6.20	—	—	57.3	—1.10
7.94	—	—	57.3	—0.63
8.03	—	—	57.3	—0.71

dass das Kasein bei gleichen Konzentrationen von Piridin dieses in grösserer Menge als Kalium-Kaseinat bindet, was die vorherige Vermutung bezüglich der Piridinsorption in Anwesenheit wie in Abwesenheit von KOH Kaliumhydroxyd bestätigte.

Aus denselben Gründen wie bei Anilin betrachten wir die Piridin-Sorption durch Kasein aus Laugenlösungen als eine Molekülsorption des organischen Stoffes. Wie die von uns aufgestellten Versuche zeigten, quillt das Kasein merklich in reinem Piridin, was von einer solvatationsartigen Wechselwirkung zwischen ihnen zeigt. Dieser Umstand veranlasst uns, die molekulare Piridinsorption als Eiweissolvatation zu betrachten.

Die S-artige Sorptionskurve im System Kasein-Wasser-Piridin, die eine «positive» und «negative» Piridinsorption ergibt, ist ihrer äusseren Form nach den Kurven für die Adsorption aus Lösungen auf Kohle und anderen Absorbenten [4] ähnlich (Adsorption in einem dreikomponenten System). Diese Kurve weist darauf hin, dass Piridin und Wasser gleichzeitig von Kasein sorbiert werden. Die Verringerung der Piridinkonzentration in der äusseren Flüssigkeit geht dann vor sich, wenn das Verhältnis der sorbierten Piridinmenge zur sorbierten Wassermengen grösser ist, als dasselbe Verhältnis in der für das Kaseinauflösen benutzten Mischung (positive Γ-Werte). Im umgekehrten Falle findet eine Zunahme des Piridingehalts in der Gleichgewichtsflüssigkeit im Vergleich zur Ausgangslösung statt (negative Werte der Piridin-Sorption). Bei der Gleichheit dieser Verhältnisse geht keine Änderung der Piridinkonzentration in der Gleichgewichtsflüssigkeit vor sich und die Sorptionskurve durchschneidet die Abszissenachse [5].

Im System Kasein-Wasser-Piridin blieb eine Änderung der Piridinkonzentration in der äusseren Flüssigkeit aus, wenn diese Konzentration in der Lösung gleich 4.34 mol/l war. Piridin und Wasser werden anscheinend in verschiedenen Gruppen des Kaseinteilchens sorbiert. Dafür spricht die Tatsache, dass das Kasein in einzeln genommenem Wasser und in Piridin quillt, während es sich in wässrigen Piridinlösungen löst.

Laboratorium für Kolloidchemie.
Chemische Abteilung
des Staatsinstituts für experimentelle Medizin.
Moskau.

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GEOCHEMISTRY

ON THE GENESIS OF THE NOVO-TROYTZKY IRON ORE DEPOSIT OF THE KHALILOV TYPE

By G. I. THEODOROVICH

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The Novo-Troytzky iron ore deposit lies in the Orsk district of the Chkalov region, 5 km NE of Novo-Troytzky settlement. So far this deposit was not subjected to any special study.

A number of investigators considered the Khalilov iron ores as a whole or only in their lower part as a peculiar ancient weathering crust of serpentinites. Conversely, A. D. Archangelsky ([1],[2]), P. L. Bezrukov and A. L. Yanshin ([3]) and V. P. Krotov ([4]) advanced an opinion as to the sedimentary genesis of the Khalilov deposit.

The deposit in question is located near the Eastern borders of the Baymaksky synclinal zone, being limited in the S, E and N by serpentinites and Upper Silurian rocks. It belongs to the Lower Jurassic system; to the west of it and partly within the area of the deposit itself non-metalliferous rocks are also to be found.

The investigation of the deposit in hand conducted by the author in 1937—1938 led to ascertaining its normal sedimentary—by no means residual—origin, this being also true of other deposits of the Khalilov type.

1. The boundaries between the ore body and the underlying serpentinites are more or less sharply marked out. The iron ores overlie different horizons or various products of the ancient weathering crust of serpentinites, which precludes the possibility of regarding the iron ores of the Khalilov type as an ancient crust of serpentinite weathering embedded «in situ».

2. The ores are usually built up either of ferruginous chlorite, or of hydrohetite, or of hydrohaematite, or else by all these three components together.

3. A cross-section of an iron ore bed of the Khalilov type is characterized by having three different kinds of horizons, which is particularly manifested in the case of the Novo-Troytzky deposit.

3a. The lower horizons (2—2.25 m) are built up of thin disperse micro-scaly ores which in their lower division posses a thinly laminar texture, passing to a coarsely laminar texture in the middle portion, while in the upper part they are found to be indistinctly or even non-laminar. These micro-scaly ores have always the same content of this or other kind of serpentine-nontronite debris and also contain small fragments of chromespinelides. Among these ores the hydrohetite-chlorite and hydro-haematite-chlorite varieties are prevailing.

3b. The middle horizons (1.0—2.2 m) are represented by micro-scaly ores which, unlike the lower ores, contain appreciable amounts of oolites and

oolitoids of ferruginous chlorites as well as hydroxides of iron, separate beans and fine ore debris.

3c. The upper horizons (3.4—4.6 m) of the ore deposit are built up of oolite and oolitoid-oolite ores which, with serpentine-nontronite material being as a rule absent, are characterized by an abundance of oolites and oolitoids of ferruginous chlorites as well as by the hydroxides of Fe, to which iron ore beans must also be added. Among these ores the following are found: hydrohetite-chlorite ores, chiefly of the chlorite variety and hydrargyllite-hydrohetite-chlorite ores. The balance of oolite ores, distinguishable by their considerable content of beans, are already to a great extent hydrohaematite-hydrohetite-chlorite formations.

Fragmental ores (sandstone conglomerate ores are liable to build up separate interlayers within different zones of the ore body and, thus, they occupy a separate position (conglomerates usually do this in the upper horizons only).

4. The author has discovered in the Novo-Troytzky deposit a new type of Khalilov ores, namely, sandstone martite-chromespinelide-chlorite ores. The bulk of this ore consists of small debris of chromespinelides which are surrounded by borders of magnetite, partly passing into haematite. Plus to this, there are also to be found grains either entirely built up of magnetite, or partly metamorphozed into haematite. Ferruginous chlorite is located among the just described ore grains.

5. The availability within the ore body of interlayers of fragmental ores is indicative of the sedimentary genesis of Khalilov ores; inasmuch as these interlayers occur also in the lower horizons of the ore body, the normal sedimentary (not residual) genesis may—from this viewpoint too—be extended to the whole mass of the ore body.

5a. This same assumption is also borne out by the presence in all these types of ores of these or other fragmental particles: metalliferous (hydroxides of Fe, chromespinelide, haematite, magnetite) or non-metallic (mainly serpentines and nontronites: sometimes also quartz, microcline, sericite, plagioclase and other varieties).

6. The normal sedimentary genesis of the ores of the deposit we are concerned with is also confirmed by the finds in them of wood fragments substituted by ferruginous chlorite, while in other deposits of the Khalilov type the same fact is evidenced yet more frequently by the presence of fossilized wood.

7. The debris found in the ore bed represent the products of the washing-out of the ancient crust of serpentinite weathering (sometimes the crust weathering of other rocks too) and also the washed- out materials of the ore body itself (sometimes also of adjacent facies).

8. Ferruginous chlorites occur abundantly within the ore bed; microscopic observations (textures, chloritized wood) show them to be chemical precipitates.

9. The hydroxides of Fe have a different origin: a) they may have partly fallen out of true or colloidal solutions in the waters of the given drainage area; b) in a certain part, they may represent mechanical precipitates; c) a certain—and apparently a considerable—part of hydrohetite arose in result of secondary processes in the development of ferruginous chlorites.

10. Hydrargyllite, as shown by examination of the micro-sections of the minerals, became segregated*—though in different quantitative propor-

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* 5% KOH extractions showed that in aluminaceous ores opal is absent. Therefore, the falling out of hydrargyllite is probably caused by an excess in Al_2O_3 content relatively to SiO_2 which becomes completely fixed in ferruginous chlorite.

tions—together with ferruginous chlorite at different moments of the diagenesis, appearing, thus, to be a syngenetic formation.

Summing up the aforesaid, it will be possible to give the following rough scheme underlying the processes of formation and secondary changes in Khalilov iron ores.

Khalilov iron ores are normal aqueous sediments. The material of which they are built up represents partly a mechanical precipitate, though for the formation of the major part chemical processes are clearly responsible. The formation of the ores took place in the littoral regions of either a single large water body or a whole system of lakes.

The nearly total absence of calcite in the ores of the Novo-Troytzky deposit permits to maintain that the ore sediments in question arose under conditions, characterized, as a general rule, by such magnitudes of pH which did not favour the precipitation of $CaCO_3$. Under the conditions available $CaCO_3$ could not fall out of the solution while all incidental calciferous organogenecus and fragmental material became dissolved.

The availability of Fe in the ferrous form (within the ferruginous chlorites) leads us to the belief that some kind of organic substance which had no time to decompose (on the surface of the bottom) had got into the silt, this substance being liable to reduce part of the ferric Fe to the ferrous state.

Those components of the original sediment which were brought in mechanically, represent small fragments, mainly of the products of weathering of the serpentinite crust.

The greatest part of the material which builds up the body is of chemical origin. In this way, i. e. syngenetically, there made their appearance the ferruginous chlorites, the bulk of the hydroxides of iron and the hydrargyllites.

Ferruginous chlorites and hydrargyllites were formed in different amounts at various moments of the diagenesis, namely: the bulk of the ferruginous chlorites appeared evidently previous to the beginning* of the falling out of the bulk of hydrargyllite, this latter corresponding to a more advanced moment in the diagenesis. However, a certain part of the ferruginous chlorite appeared almost simultaneously with the bulk of the hydrargyllite, while a portion of the hydrargyllite came into being at the same time as the bulk of iron chlorites did.

The ferruginous chlorite is always formed in course of the diagenesis process. Depending upon the stage at which the conditions, necessary for the formation of ferruginous chlorite, will be likely to appear—whether this be at a moment of greater or lesser condensation of sediments—we shall have respectively either ferruginous chlorite building up oolitoids and oolites, or else, a rock which fails to form any such texture. In a but slightly condensed sediment the formation of oolitoids and oolites of ferruginous chlorites could have taken place. Contrariwise, such formations of ferruginous chlorite could not occur in the case of the appearance of chlorites in a strongly condensed sediment.

Thus, an ore of the Khalilov type is essentially one of chemical origin, yet the peculiarities of its mineralogical composition and texture may be accounted for by internal regroupings running inside the mass of the accumulating sediments.

Further on, due account should be taken of the phenomena of denudation of an ore body within the very period of ore formation (Lower Jurassic) connected with subterranean wash-out, or the temporary outcropping of separate sections of the ore body from under the water. The washing out

* Which fact took place during the deposition of the upper beanshaped oolitic ores.

of the ore might have taken place not only during the Lower Jurassic period, but also within the Middle Jurassic period and later.

The described case of martitization of one of the types of Khalilov ores speaks apparently in favour of an ancient surface weathering in a warm climate which might, possibly, have been the state of things prevailing both within the Jurassic period and later on. The martitization process failed, however, to reach its termination, probably on account of the short-time existence of the conditions contributing to its development or perhaps in connexion with the fact that the underlayer subject to martitization was located at a certain depth (true, not a very great one) from daylight.

To the number of obviously secondary processes associated with weathering which were more or less likely to change the original appearance of ores belongs, in the first place, the process of chrominization of ferruginous chlorites.

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GEOCHEMISTRY

PART TAKEN BY CLOSE PACKING OF CRYSTALS IN THE DIFFUSION OF HELIUM

By E. K. HERLING

(Communicated by W. G. Khlopin, Member of the Academy, 26. V. 1939)

Works published within the last years have shown (1) that the main bulk of investigated minerals and rocks are unfit for identification of age according to the helium method, on account of a considerable loss of helium by them*. Now, the question arises as to what the reason for this loss of helium by minerals and rocks is; and whether it cannot be possibly referred to some peculiarities of these minerals structures. The author believes that in the light of the modern idea of diffusion, allowance being made for the structure of the minerals studied, it will not only be possible to explain the helium losses but also to give a new trend to a further development of the helium method of age determination.

According to the hypothesis advanced by A. F. Joffe (2) and later on developed by J. I. Frenkel (3), the diffusion of ions or atoms in crystals proceeds within the intercrystalline space, the diffusing atom bounding from one unit cell to another. Each such jump, apart from the activation of the diffusing atom, is also associated with the activation of the atoms or ions of the solid which thwart the motion of the atom over the intercrystalline space. It is to be supposed that the dimensions of the intercrystalline space exert a material influence upon the velocity of helium transport. In a crystalline lattice with a loose structure in which the dimensions of the free intercrystalline space are great, the diffusion of helium should proceed with greater ease, since this process must evidently be connected with a lower activation of atoms than in the case of crystals with close packing. Accordingly, there ought to be a greater loss of helium with loose and non-compact crystalline structure.

The question now arises: what is the structure of the main mass of rock-forming minerals, in which the bulk of helium lies originate?

In Table 1 are given data on the closeness of packing of the main groups of rock-forming minerals taken chiefly from Schiebold's article (4). Only for a few of them calculation was made by the author himself on the basis of the respective data of X-ray analysis borrowed from the literature (5). As a criterion for measuring the closeness of packing, the volume corresponding to one atom oxygen is taken. For the theoretically closest packing per one

* Urri's data are, as this became known in 1939 from the Reports of the American Committee on Geological Time, erroneous and should be reduced 1.5—2 times.

Table 1

Name	A^3 per 1 atom of oxygen	Name	A^3 per 1 atom of oxygen
Nepheline	22.7	Olivine group	18.3—21.3
Feldspar group	21—23.0	Quartz	18.7
Mica group	19.3—20.4	Garnet group	15.8—18.1
Chlorite group	19.3	Magnetite	18.5
Melilite group	21.8—22.6	Calcite	20.3
Amphibole group	18.3—19.8	Arragonite	18.7
Pyroxene group with the exception of spodumenes	17.4—21.1	Dolomite	18.0

atom of oxygen the volume of 13.9 A^3 has, as is well-known, been established. It may be readily seen from the table that the bulk of rock-forming minerals are rather loose structures. Particularly loose structures belong to feldspars, nephelines, mica and minerals of the melilite and chlorite groups. The same holds to a great extent true in respect of the majority of amphiboles and pyroxenes with the exception of spodumene, enstatite, bronzite and some other minerals for which the closeness of packing is medium. At the bottom of the table data are given for the closeness of packing of calcite, arragonite and dolomite, which show that these minerals display a sufficiently open structure. The limestones examined by L. V. Komlev and the author exhibited a considerable loss in helium fluctuating for individual samples from 60 to 95%. Thus, the main bulk of rock-forming minerals, with the exception of a few minerals of the garnet group, are no closely packed structure, having a large free space unoccupied by ions. The diffusion of helium in such crystals cannot be sufficiently thwarted and the amount of this gas lost by them is, therefore, large. The closeness of packing of crystals plays, indeed, a decisive part in the loss of helium by minerals, then, with its increase, the amount of lost helium should necessarily diminish.

In Table 2 are to be found the results of the determination of the age of some minerals after the helium method and also data on the closeness of their packing. It will be seen from this table that for the loosest structures, such as albite, labrador and quartz, the amount of helium lost constitutes 75—90%. Somewhat more closely packed minerals, as dolomite and haematite, show a lesser loss of helium. On the basis of these data one should assume that the minerals with a packing close to the theoretical, or but little differing from the latter will prove appropriate for age determinations by the helium method. In such minerals the free intercrystalline space is reduced to a minimum and accordingly diffusion of helium may be anticipated.

In Table 3 are to be found data for several minerals with the closest packing for which we deemed it necessary to carry out age determinations according to the amount of helium accumulated in them.

It will be seen from the Table 3 that the closest packing belongs to corundum, polyanite, topaz and chrysoberyl. For these minerals the closeness of packing is almost terminal. Niobite, cyanite, rutile and a number of other minerals represented in the table are likewise close structures. It should be taken into consideration that the presence of appreciable amounts of extraneous inclusions in crystals makes their structure less close which may involve a appreciable loss of helium in them. Due account has been taken of this circumstance. In selecting rocks for sampling it is necessary to choose

Table 2

Specimen and place of sampling	Closeness of packing (A^3)	Geologicel age	Age according to He in terms of 10^6 years	% loss of helium	Analyst
Albite, Quinsy, Mass., USA	21.6	Devonian	49	83	Keevil
Labrador, USA	21.4	Pre-Cambrian	101	80—90	»
Limestone Bashkiria, USSR	20.3	Permian	8	95	Herling a. Komlev
Limestone of Po'onetz Kokul elevation, USSR . .	20.3	»	22	88	»
Quartz, Quinsy, Mass., USA	18.7	Devonian	66	75	Keevil
Sphene, Arendal, Norway .	18.4	Pre-Cambrian $1.3 \cdot 10^8$ years	352	73	Strutt
Sphene, Tweedstrand, Norway	18.4	»	409	68	»
Sphene, Renfrem, Ontario .	18.4	Lower pre-Cambrian $1.5 \cdot 10^8$ years	600	60	»
Dolomite, Karelia	18	Lower Proterozoic	577	40—50	Verestchagin, Herling, Starick
Haematite, Antrim, Irland	16.7	Posteocene	25.5	40—50	Strutt
Haematite, Caen	16.7	Devonian	120	60	»

Table 3

Minerals	Volume per 1 atom of oxygen in A^3	Cleavage	Fracture
Corundum	14.05	Absent	Shell-like
Polyanite	13.9	Complete	Uneven
Rutile	15.46	»	»
Chrysoberyl	14.18	Incomplete	Shell-like
Topaz	14.25	Complete	»
Cyanite	15.05	»	»
Pyrope	15.8	Incomplete	»
Almandine	15.8	»	»
Niobite	14.9	Medium	»
Magnesite	15.0	Complete	Uneven
Spinel	16.3	Incomplete	Shell-like

a piece which would be as free as possible from foreign inclusions. Moreover, the ability of certain minerals to pass into the metamict condition can exercize an essential influence upon loss of helium in them. One may assume that zircon is partly affected by this transformation, which fact is according to Strutt, inspite of the rather close structure of this mineral, responsible for a considerable loss of helium. The presence of clearly pronounced cleavage in a mineral is another factor contributing to loss of helium since the cohesion of ions or atoms, while being the lowest both perpendicular to the plane of cleavage and along the distances between the planes of the lattice, proves here, as established by Bravet, to be the strongest. In the light of the above, one should believe that the absence of cleavage in certain minerals ought to have a favourable effect upon the helium conservation. The experimental material at hand brings strong evidence to

bear in favour of this view, since results that agree with geological data were obtained only with minerals deprived of cleavage or with incomplete cleavage.

These results are recorded in Table 4.

Table 4

Specimen and place of sampling	Geological age	Age according to He in terms of 10^6 years	Probable loss of He (%)	Cleavage
Khlopinite, Transbaikal, Hylock	Jurassic—Permian	132	12—25	Absent
Eshinite, Ural	Permian—Carbonif.	210	< 10	»
Samarskite, Ural . . .	Permian—Carbonif.	237	< 10	Incomplete
Loparite, Khibiny . . .	Carbonif.—Devonian	280	< 10	Absent

Briefly summing up the above stated, the following conclusions can be made:

1) Loose crystalline structures are liable to lose helium easily, wherefore they are unfit for identifications of geological age.

2) Reliable results may be obtained only with minerals with close packing, which would be as free as possible from inclusions, subject to no kinds of transformations, in particular to metamictoism, and more over deprived of cleavage.

Work in this direction is in progress at the Radium Institute of the Academy of Sciences of the USSR.

Radium Institute.
Academy of Sciences of the USSR.

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GEOCHEMISTRY

MOLYBDENUM IN MINERAL, MINE AND SURFACE WATERS

By I. P. NOVOKHATSKY and S. K. KALININ

(Communicated by A. E. Fersman, Member of the Academy, 2. VI. 1939)

Molybdenum has been rarely reported to be found in waters. Data on the molybdenum content in thermals of France and Spain have been given by J. Bardet (1) and Pina de Rubies (2) respectively. The majority of analyses of mine waters contains no data pointing to the presence of molybdenum. Molybdenum content of waters is, however, of considerable interest when solving the problem as to the concentration of molybdenum in the zones of oxidation of certain lead deposits in the form of the mineral wulfenite; the same may be said of its accumulation in sedimentary rocks, in particular under the form of ilsemanite.

From the spectroscopic examination of the dry residue of different types of water carried out by the authors, one may arrive at a conclusion that molybdenum is rather frequently contained in them. The highest molybdenum content has been shown by the waters of the thermals of the Transilian Ala-tau Range (Tyan-Shan). In all the water samples taken for analysis from sixteen thermals molybdenum is present in quantities amounting to 0.06 per cent (calculated for dry residue which makes up 0.27 g per liter). About the same amounts of molybdenum have been found in the thermals of the Kopal-Arasan (Djungara Ala-tau). Smaller quantities have been detected in the water of Batalinsk and Slaviansk mineral springs. We failed to find molybdenum in the waters of Essentuki, Smirnov and Izhevsk springs even though we had recourse to spectroscopy.

Molybdenum has been detected in some mine waters as well as in the waters of the springs near the deposits.

Spectroscopically it has been identified in the water from shafts of the Kownrad copper deposit. The amount of molybdenum makes up some thousandth of per cent (per dry residue, equal to 0.3—0.7 g per liter). In the mine water of the Uspensk copper deposit molybdenum has been found at a depth of 120 m and more; while in two samples taken from higher horizons it proved absent. The waters of the Dzhekazgan copper deposits (nine samples) and of the Maikain gold deposit (four samples) have also been analyzed; molybdenum failed to be found, though it is present in the ores.

Molybdenum has been found in the water of a well sunk in calcareous conglomerates at the polymetallic deposit Kyzyl-Espe; whereas in the waters from the mine of the central area of the same deposit it failed to be detected.

Neither was it revealed in the waters of the flooded mines of the polymetallic deposit Gulshad. Negligeable amounts of it are spectroscopically detected in the springs in the vicinity of Tashkent (in six samples out of nine).

It is of interest that neither waters of the salt lakes of Kazakhstan, subjected to analysis, nor those of the sources feeding the two first lakes, showed any traces of molybdenum. It has not been found in the borehole waters of the Ural-Emba region either.

The above data point to that molybdenum is widespread in waters, its content largely varying with the type of the latter.

The highest molybdenum content has been observed in waters of thermal springs connected with granites and diorites. It should be noted that number of primary molybdenum deposits are located in the Transilian Ala-tau. In the surface waters running down the Transilian Ala-tau range it has been observed, too. It is rather peculiar that Pina de Rubies reports the presence of molybdenum only for those thermals which spring of granites.

The second place with regard to their molybdenum content belongs to waters connected with copper or polymetallic deposits containing molybdenum. The presence of molybdenum in the waters of Kownrad may be accounted for by the wide distribution in them of molybdenum under the form of molybdenite, as it is the case in other deposits of this type.

In the same way may be explained the presence of molybdenum in the mine waters of the polymetallic deposit Kyzyl-Espe in the oxidized zone of which molybdenum is rather widespread under the form of wulfenite.

The connexion between the presence of molybdenum in surface waters and the molybdenum containing deposits is confirmed by the analyses made by N. M. Khitarov and L. I. Ivanova, who have found molybdenum in the waters of a spring draining the Nuratin deposit of powellite.

Of interest is the finding of molybdenum in the mine waters only of certain horizons, which is, evidently, closely connected with the hydrogen ion concentration.

In the waters of saline stagnant basins, as well as in oil waters molybdenum is absent, on account of its earlier precipitation. Goldschmidt, however, suggests for sea water a molybdenum content of 0.7γ (per 1 kg of water).

The decrease in molybdenum content in surface waters may be accounted for, apart from its natural dispersion, also by the adsorption of molybdenum by freshly precipitated iron and manganese hydroxides. Molybdenum can also be adsorbed by secondary sulphides in the zone of sulphide enrichment of metallic deposits.

Kasakhstan Branch.
Academy of Sciences of the USSR.
Alma-Ata.

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METEORITICS

NEW FINDINGS OF THE JOVTNEVY METEORITE

By E. L. KRINOV

(Communicated by W. I. Vernadsky, Member of the Academy, 28. V. 1939)

Since the publication of the paper describing the fall of the Jovtnevy stone meteorite (1), two more individual specimens (the 5th and the 6th one) of the same meteorite were discovered. Both specimens were found by N. I. Grenetz, tractor operator of the K. Marx Collective Farm, on the 8th of April 1939 in course of spring ploughing, approximately within 1.5÷2 km northwards from the spots of finding of the 3rd and the 4th specimens. The 5th specimen (Fig. 1), weighing 21745 g, was lying in an autumn ploughed field, in a pit produced by its fall 40 cm deep. The meteorite had a semi-oriented shape and was covered with a crust, having lost small fragments only in a few spots. These fragments had evidently been broken off from the main mass in mid-air, but already after the flight had become impeded. Some other fragments had apparently also been broken off by force of the impact against the ground. No fragments were, however, discovered at the place of finding. Among all the specimens of the meteorite shower at Jovtnevy, this one is so far the only entire one and the biggest of all in weight*.

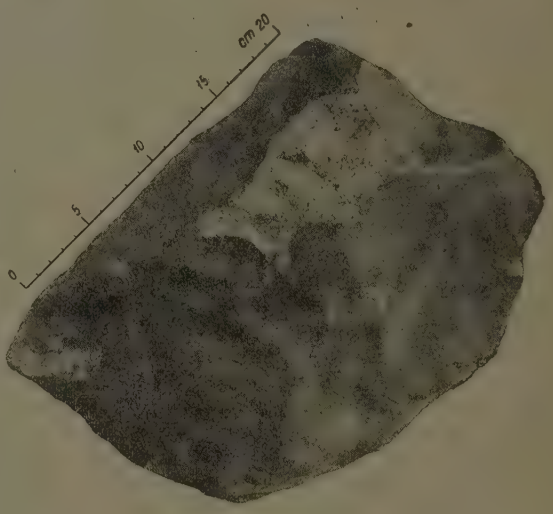

Fig. 1.

The sixth (the smaller) specimen lay on the surface of the ground at about one kilometer eastwards from the preceding one. It had been partly broken to pieces by local people; now there remains only the bulk of the meteorite weighing 9920 g, and 12 fragments of an aggregate weight of 2953.40 g. Thus, the weight of all the parts of this specimen constitutes

* The first, the largest one, weighing 32 kg, was broken to pieces.

12873.40 g. By putting all the fragments together the original shape of the meteorite may be almost completely restored (Fig. 2). The weight of all the missing fragment probably does not exceed 200 g.

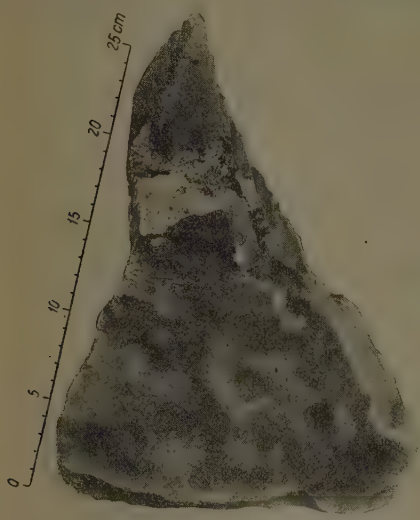

Fig. 2.

All the parts of both specimens were delivered to the meteorite collection of the Acad. of Sciences of the USSR by the author who made on behalf of the Committee on Meteorites of the Academy of Sciences an inquiry about the circumstances of the findings and collected additional data concerning the fall. Somewhat later the author received from the inhabitants 3 fragments of the first specimen, of an aggregate weight of 174.70 g, and also 6 fragments of a 3rd specimen weighing 232.00 g. Besides this, one more fragment of the 2nd specimen, weighing 120.9 g, was received directly by the Committee on Meteorites, having reached its destination by parcel post.

Thus, by the present time the Collection of the Academy of Sciences has received:

44	fragments	of	the	1st	specimen	of	a total	weight	of 9410.40 g
3	»	»	»	2nd	»	»	»	»	» 443.79 »
15	»	»	»	3rd	»	»	»	»	» 18694.62 »
1	»	»	»	4th	»	»	»	»	» 2736.00 »
1	»	»	»	5th	»	»	»	»	» 21745.00 »
									(a whole specimen)
13	»	»	»	6th	»	»	»	»	12873.40 g
								Total weight	65893.21 g

Apart from gathering fragments of the meteorite, the author, during his latest (third) journey to the spot of the fall, obtained from the eyewitnesses highly valuable and rather abundant material on the fall of the meteorite. Owing to this at present we dispose of descriptions from a number of localities lying within a radius of up to 6 km from the spot of the fall.

Preliminary study of this material permits of assuming that several rather voluminous masses (of the order of the found one) might have been fallen westward from the farm Jovtnevy, while somewhat smaller specimens should be sought to the south from the village Prechistovka. Besides this, the finding of a yet larger mass than the first specimen may be possible to the southeast from the place of the finding of that piece. And, finally, a large part of the 4th specimen is still missing.

These parts of the meteorite may yet be discovered during the autumn harvesting or ploughing of fields.

Committee on Meteorites.
Academy of Sciences of the USSR.
Moscow.

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GEOLOGY

ON THE CONTACT METAMORPHISM OF PHOSPHORITES

By P. L. BEZRUKOV

(Communicated by A. N. Zavaritsky, Member of the Academy, 19. V. 1939)

No cases of thermal metamorphism of sedimentary phosphates in contact with igneous rocks have been so far reported in geological literature. Suffice it to say that in none of the new cumulative works devoted to metamorphism in general and to that of sedimentary rocks in particular, any attention whatever was given to the problems of contact metamorphism of phosphorites. Neither have these problems been treated in works dealing with the geochemistry of phosphorus in nature, or with the geology of phosphate ore deposites. The explanation of this fact should evidently be sought in that the phosphorites are distributed chiefly over regions where volcanic activity is developed to a slight degree, if at all.

However, some metamorphic rocks rich in apatite (e. g. the quartz-diopside rocks of the Sludyanka in Transbaikalia, the apatite-bearing shales of the Iron Mountains in Czechoslovakia, etc.) have been more than once considered by individual authors as altered sedimentary deposits. Inasmuch as the metamorphism of such rocks is of regional rather than contact character, nobody has as yet succeeded in tracing the transition from these to normal primary phosphate sediments.

In 1937 the author was working at the north-eastern branch of the Kara-Tau Range (South Kazakhstan), busy to investigate new rich deposits of Lower Paleozoic bedded phosphorites(1); his purpose was to find out the effect of Caledonian granite intrusions developed in the same region and breaking through the Lower Paleozoic upon the phosphate beds.

Preliminary inspection was sufficient to show that near the granite intrusion located at the Maly Karoy anticline between the Kok-tal and Kyrchabakty rivers, the Lower Paleozoic rocks are suffering intense metamorphism. The Lower Silurian dolomites overlying the phosphate beds, pass to marbles, Cambrian shales and sandstones, while those overlain are transformed into different metamorphic shales. However, the author did not succeed in observing the alteration of the phosphorites themselves owing to their insufficient exposure, whereas at a distance of 0.5 km from the granites they still preserve their normal habit. Nevertheless, the author advanced the assumption that in the closest proximity of the granites the phosphorites must certainly pass into bedded apatite rocks along the strike(2).

In the course of further prospecting work at the Kara-Tau in 1938 the author came across an environment exceptionally favourable for the investigation of contact metamorphism of phosphorites at another anticline, the Teshiktass, within the area of the Kok-tal River.

At the core of the Teshiktass anticline Cambrian sandstones and argillo-siliceous shales crop out to the surface, upturned or steeply dipping to the north-east. At the north-eastern limb of the fold they are successively overlapped first with a small packet of «lower» dolomites (thickness up to 5 m), then with phosphate beds (16—25 m) and later on with a thick calcareous-dolomitic series of the Lower Silurian.

At the north-western termination of the fold the phosphate beds are composed in their lower portion of black slightly phosphotized tabular flints, in the upper portions—of dark-grey bedded phosphorites, showing under the microscope a fine-grained oolitic texture. Among the phosphorites are present both poor siliceous and carbonate (dolomitized) varieties with 15—20 per cent P_2O_5 and high-grade varieties containing up to 29—32 per cent P_2O_5. The latter make up the upper part of the beds, their thickness attaining 3.5 m. They are overlain first by tabular and then by massive dolomites.

Further to the south-east, at the right bank of the Teshiktass ravine, the rocks composing the anticline are broken through by an intrusion of pinkish-grey biotitic plagiogranites. Over a distance of about 1 km the outcrops of the phosphate beds are stretching parallel to the edge of the intrusion. The granites contact sometimes with Cambrian shales, sometimes with «lower» dolomites, and occasionally with rocks of the phosphate beds themselves which are steeply dipping north-eastward from them. At the south-eastern termination of the fold the granite field grows wider, while its margin is merging into the overlying dolomites.

The contact effect of the intrusion is expressed in recrystallization of the rocks, alteration of their microstructure, and in the appearance in them of a number of new minerals. The sequence of occurrence and the thickness of individual horizons of the section described are preserved in their general features.

The most interesting alterations are observed in the rocks of the phosphate beds. Owing to the termal effect of the intrusion, the phosphorites are subjected to metamorphism, and are replaced by apatite beds. These are light-grey, yellowish or pinkish finely-crystalline rocks made up essentially of small (1.01÷0.1 mm) apatite crystals with a varying admixture of calcite, secondary quartz, serpentinite (chrysotile), muscovite and some other silicates, as well as iron oxides. The organic matter from which the phosphorites receive their dark colour, disappears in those rocks. Occasionally among the apatite rocks appear bands and irregular lenses of diopside and chlorite-micaceous rocks. In one case, in a fissure among apatite rocks there were found galenite crystals.

To understand such a various and peculiar composition of these rocks, and in particular the presence in them of serpentine, pyroxene and some other magnesial minerals, it is necessary to take into account that the phosphorites occur among carbonate (dolomites) and siliceous sediments, containing, in the form of impurities, dolomite, chalcedony and quartz.

The presence in apatite rocks of galenite and of certain other minerals (in particular micas) points to the fact that thermal metamorphism was accompanied with an admixture of volatile components, carried in by the intrusion.

No traces of the primary structure of phosphorites have been preserved in the apatite rocks in the closest proximity of granites. The crystals of apatite form elongated prisms sometimes coming into contact with one another, sometimes dispersed throughout the calcitic ground mass. Traces of the original lamination of the rocks are occasionally observable from the alternation of bands richer in calcite or quartz. In spite of the variability of the composition of apatite rocks, the main apatite layer may be readily traced among

them, his thickness being from 2 to 3.8 m. Analyses of furrow samples taken at the point of maximum thickness of the layer, have shown a P_2O_5 content of 21.3 per cent. Individual samples of apatite rocks contain as much as 32 per cent of P_2O_5.

Further off the intrusion to the north-west, typical apatites are replaced by very interesting transitional rocks, in which the relict grained structure of phosphorites has been preserved, while the phosphate grains have been replaced by aggregate crystals of apatite. Alongside of apatite grains, grains of common microcrystalline and colloidal phosphate make their appearance in these rocks. Similar transitional varieties of apatite crystals have been encountered 1.5 km from the margin of the granite field. In so far as it is scarcely probable that the termal effect of intrusion can be observed over such vaste an area without loosing its intensity, one is bound to assume that the surface of intrusion is flat dipping, and that along the vertical the distance from it is here much less. Still farther from the granites the rocks described are replaced by normal phosphorites.

The Cambrian siliceous-argillaceous shales underlying the phosphate beds in the zone of metamorphism pass into quartz-micaceous schists, «lower» dolomites pass into dolomitic marbles, while phosphate flints are transformed into finely-crystalline quartzites. The overlying Silurian dolomites are replaced by marbles, occasionally containing serpentine pockets (ophicalcites). Coatings of green copper are observed in marbles along the contact line with granites; in the lowermost part of the marbles (5—10 m) are disseminated apatite crystals, metasomatically replacing calcite. The finding of these crystals permits of suggesting that recrystallization of phosphate was partly accompanied with sublimation. The process of sublimation, as under artificial conditions, seems to have been favourably influenced by the presence of silica in these rocks.

In conclusion it should be mentioned that the apatites in Teshiktass form a rather extensive accumulation and may evidently possess high economic value. The reserves are estimated at several million of tons. However, this deposit is of still greater scientific interest, since it offers the possibility of studying in detail the phenomena of contact metamorphism of phosphorites and of their transition into bedded apatites. From this standpoint the Teshiktass deposit is unique, having no analogous all over the world. It stands to reason that special thourough investigation of these deposits is urgently required.

Institute of Fertilizers and Insectofungicides.
Moscow.

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MINERALOGY

NEW FINDINGS OF MINERALS IN THE MIDDLE COURSE OF THE SOUTH BUG RIVER

By V. A. SAVOSTIANOV

(Communicated by A. E. Fersman, Member of the Academy, 22. V. 1939)

The ancient crystalline rocks of the middle course of the South Bug River, frequently cropping out to the surface and only slightly covered up by a thin layer of Quaternary and occasionally of Tertiary rocks, are composed of a very involved complex of rocks of the charnokite-norite range (the so-called charnokite-bughite series) (1).

Over a distance of 30—35 km, from the villages of Strijevka and Pyatnichany to the locality Gnivan, numerous passings of the rock to another have been observed together with clearly manifested differentiation and assimilation processes.

The processes of differentiation manifest themselves in the presence of epimagma along with mesomagma. Epimagma is characterized by a higher acidity than the deep-seated batholite horizons, a greater mobility and an accumulation of volatile components.

Owing to the direct contact with the gneiss roof, the processes of assimilation are concentrated with in the epimagma. These processes are as follows: under the influence of the acid, mobile, active epimagma rich in volatile components, very marked changes take place in the xenoliths of the pyxorene-plagioclase gneiss, up to the formation of different mixoliths (hybridized granites, migmatites and injected gneisses); in these changes have been observed for dark-coloured minerals, proceeding in accordance with Bowen's reaction scheme.

The typical epimagma is represented by pink and partly light-grey aplitoidal and aplitopegmatitic granite and pegmatitic and aplitic vein formations.

The mesomagma consists of a number of rocks from pyroxene granite to quartz and sometimes even quartzless norite.

A microscopic and macroscopic study of the rocks enabled us to establish five minerals new to this region.

1. In the coarse-grained pegmatoid hypersthene granite a considerable amount of pyrrhotine phenocrysts has been encountered.

The pyrrhotine is clearly anhedral; it seems to cement large crystals of feldspar, quartz, biotite and hypersthene, occasionally penetrating into large crystals of feldspars along the fractures. Such a character of filling the fractures and interstices between individual minerals testifies to a rather late isolation of the mineral from the epimagma. In such a case

pyrrhotine is to be regarded as a product of pegmato-pneumatolitic processes, corresponding to Fersman's C-phase (2).

In other cases pyrrhotine is observed as a contact mineral in xenoliths of the biotite-plagioclase gneiss highly enriched in garnet.

2. Chalcopyrite phenocrysts have been encountered in the xenoliths of biotite-plagioclase gneiss together with pyrrhotine.

3. In quartz-feldspar veins, containing very large garnets, intersecting grey granites, small molybdenite phenocrysts have been encountered.

Proceeding from that in the region under description no hydrothermal manifestations have been observed, molybdenite is to be regarded as an early mineral connected with the quartz phase of pegmatization, i. e. as a pegmato-pneumatolitic mineral, isolated at the beginning of Fersman's D-phase at 700—600°.

It would be of interest to note that in the same year the author has observed small molybdenite segregations in an injection veinlet near the station of Talnoie in the region of extensive development of the Dnieper granite bearing an aplitoidal character.

Analogous molybdenite findings made in the area of the station of Tok by G. G. Yurko show that the Ukrainian crystalline belt is molybdene-bearing.

4. Along the South Bug River in the neighbourhood of the village of Sabarov graphite has been encountered, whose formation took place in two ways:

a) Contact-metamorphically, when graphite in pure large scales has been observed in calcite bands in the calcareous silicate xenolith.

In this case the cause of graphite isolation should be sought in the effect of acid active epimagma on carbonates.

b) Pneumatolitically in the form of small scales and coatings in a pegmatite vein.

The author feels inclined to explain the appearance of graphite in the pegmatite vein by the fact that the acid granite epimagma has been enriched with carbon during the assimilation of xenoliths of calcareous silicate rocks, and later on granite has been isolated in its satellites, presenting pegmatite veins, intersecting the rocks of the charnokite-bughite series. The temperature conditions of this process are probably not very different from those suggested by Knopff (disintegration of CO_2).

5. Dark-green ferruginous spinel has been found in thin sections of a fine-grained xenolith of the garnet-pyroxene-plagioclase gneiss, highly enriched with garnet. Its formation most probably took place in a contact-metamorphic way under the influence exercised by the charnokite-bughite magna on the xenoliths of the pyroxene-plagioclase gneiss, which converted them into garnet-pyroxene-plagioclase rocks containing spinel.

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MINERALOGY

ON THE CLASSIFICATION OF SOME MAGNESIAL SILICATES AND THEIR ALUMO-ANALOGUES

By N. E. EFREMOV

(Communicated by A. E. Fersman, Member of the Academy, 22. IV. 1939)

The questions connected with the composition and classification of some magnesial silicates of the kerolite and sepiolite group and of their respective alumo-analogues—beidellite and montmorillonite—are still lacking clarity.

Some hydrous alumosilicates are frequently termed rather arbitrarily, without a thorough analysis of their constitution. Thus, under the name of «montmorillonites» are described beidellites, under that of «beidellite», alumodeveillites (4) etc. The cause of this annoying confusion should obviously be put down to the absence of an adequate classification of the argillaceous hydrosilicates, the development of which becomes, therefore, a matter of urgent necessity.

On the basis of the results of his own investigations in this field, the author feels inclined to believe that a successful solution of this question may be reached by comparing the magnesial hydrosilicates with their alumo-analogues.

This was the very principle which A. E. Fersman was the first to formulate with regard to the palygorskite group isolated by him.

The author believes this to be the most reasonable way to bring more precision into the mineralogical terms for the initial molecules, since it would permit of eliminating from the mineralogical nomenclature a considerable number of terms, the introduction of which was not justified by any necessity (5).

At present it seems to be ascertained that a considerable number of clayey minerals should be considered as intermediate members of series of hydromagniolites and hydrosyalites [(5,4) and others].

An indication of the initial molecules and of their ratios will be a sufficient factor for classification, without necessitating any special terms for the minerals to be classified.

Thus, the «centre of gravity» is transferred in such a classification from separate representatives to the initial combining molecules; it stands to reason that the latter will be much less in number.

In this respect it will be of interest to point out the existence in nature of a mineral detected by the author while studying the mineralogy of serpentinites of the North Caucasus.

This mineral was found in smal quantities among highly decayed pale-blue amphiboles, occurring in a contact zone between an acid dyke and the enclosing serpentinites. It seems to be certain that genetically it is a product of alteration of these amphiboles. From its habit the mineral is a typical

sepiolite (Meerschaum). The mineral is compact, gel-like, with a plane conchoidal fracture. Its colour is white, with a delicate creamy tinge. Hardness 1. Under the microscope sepiolite shows an interlaced fibrous structure: $N_g' = 1.520$; $N_p' = 1.510$; $N_g' - N_p' = 0.010$. Elongation positive.

Thermogram No. 1709 made with the help of a Saladin-le Chatelier apparatus shows three endothermic effects, at 150, 350 and 730° respectively.

The powdergram made in the Laboratory of the Geological Institute of the Academy of Sciences points to the presence of intense lines characteristic of sepiolite.

The chemical analysis made by M. A. Gribova is given in the table.

Oxides	Weight per cent	Molecular quantity
SiO_2	48.65	811
Fe_2O_3	0.18	1
Al_2O_3	0.44	4
FeO	Traces	—
MnO	Abs	—
CaO	3.44	62
NiO	Traces	—
MgO	24.35	609
H_2O+	13.18	734
H_2O-	9.52	528
CO_2	0.35	8
	100.01	—

From the ratio of the principal oxides we obtain the following formula of the mineral: $2.50\,MgO.3SiO_2.4.5H_2O$. Its composition closely approaches to that of the sepiolite, which is $2MgO \cdot 3SiO_2 \cdot 4H_2O$, differing from the latter by a prevalence of bases over the silicic acid, and by a certain excess of water.

When the formula is written according to Longchambon and Migeon (6), the difference stands out still more sharply:

Our mineral: $3.3MgO.4SiO_2.H_2O.5H_2O$.

Sepiolite: $3(Mg, H_2)O.4SiO_2H_2O.3.5—4H_2O$.

It may be easily seen that the value of the silico-magnesial module for our mineral is $MgO : SiO_2 = 0.83$, while in the common sepiolite it is equal to 0.65.

It should be noted that, as had already been shown for serpentinites (9) and kerolites, among the «sepiolite» minerals as well there exist varieties in which the ratio $MgO:SiO_2$ varies within a rather considerable range. An examination of the formulae of sepiolites given below * comes forcibly in support of this view:

1. Sepiolite. North Caucasus:

2.50 $MgO \cdot 3SiO_2 \cdot 4.5H_2O$, $MgO : SiO_2 = 0.83$.

2. Sepiolite** from Maryland, from Rotenzechau (3):

2.25 $MgO \cdot 3SiO_2 \cdot nH_2O$, $MgO : SiO_2 = 0.75$.

3. Sepiolite from Salinelle (11)***:

2.0 $MgO \cdot 3SiO_2\ 5H_2O$, $MgO : SiO_2 = 0.66$.

4. Sepiolite from Cabanas(11):

1.8 $MgO \cdot 3SiO_2 \cdot 5.8H_2O$, $MgO : SiO_2 = 0.60$.

5. Hypothetical mineral:

1.5 $MgO \cdot 3SiO_2 \cdot nH_2O$, $MgO : SiO_2 = 0.50$.

It was reasonable to postulate the existence of the above molecules 1 and 5 taking into account that in nature there exist both their analogues and rather numerous minerals resulting from mixtures of the above magnesial and aluminium molecules, in which $3MgO \rightleftarrows Al_2O_3$ are mutually and equivalently substituted.

Therefore we might write among others the following series composed of the mentioned initial magnesial and alumina molecules, having united them under corresponding terms:

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* The coefficients in the formulae are given in round figures.

** To this type corresponds also the sepiolite from Magador (11).

*** This type seems to be of more frequent occurrence.

1.	$Al_2O_3 \cdot 3.66\,SiO_2 \cdot 5{\cdot}5H_2O$	α - montmorillonite
	$3MgO \cdot 3.66\,SiO_2 \cdot 5{\cdot}5H_2O$	α - sepiolite
2.	$Al_2O_3 \cdot 4.00\,SiO_2 \cdot 6{\cdot}0H_2O$	β - montmorillonite
	$3MgO \cdot 4.00\,SiO_2 \cdot 6{\cdot}0H_2O$	β - sepiolite
3.	$Al_2O_3 \cdot 4.5\,SiO_2 \cdot 6{\cdot}0H_2O$	γ - montmorillonite
	$3MgO \cdot 4.5\,SiO_2 \cdot 6{\cdot}0H_2O$	γ - sepiolite*
4.	$Al_2O_3 \cdot 5.\,SiO_2 \cdot 6{\cdot}0H_2O$	δ - montmorillonite
	$3MgO \cdot 5.\,SiO_2 \cdot 6{\cdot}0H_2O$	δ - sepiolite
5.	$Al_2O_3 \cdot 6\,SiO_2 \cdot n\,H_2O$	ε - montmorillonite
	$3MgO \cdot 6\,SiO_2 \cdot n\,H_2O$	ε - sepiolite

Thus, the mineral described is a magnesial analogue of a «montmorillonite» mineral with the formula $Al_2O_3.3.66SiO_2.5.5H_2O$ **.

All the molecules of the first four series are minerals existing in nature ***, numerous intermediate members—products of their mixtures—being known for them.

In this immense world of «sepiolite-montmorillonite» mineral bodies, bound up into the palygorskite group by the theoretical conceptions of A. E. Fersman as to their constitution, science is detecting ever new representatives.

Moreover, the formulae proposed clearly reflect all the various attempts to work out new formulae for montmorillonite [this refers more particularly to American and French authors ([1], [2], [5])], these attempts having led so far to rather ineffectual dispute in this field.

By means of gradual transitions (decrease of silica) through the beidellites the hydrosyalites of the montmorillonite type are connected with the kaolinite-halloisite type ****. The molecule of ε-montmorillonite, which is really existing in nature, enters the composition of the montmorillonite described above; it is characterized by the highest silica-content. In the light of the above said it is necessary to assume the existence of its magnesial analogue which it should be expedient to term as ε-sepiolite. The probability of this molecule to exist in nature is grounded on the existence of intermediate members due to mixtures of molecules of the ε-montmorillonite—ε-sepiolite type among the Fuller-earths from Olmstead, Illinois ([2]).

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* It should be noted that the hypothetical molecule $3MgO.\,4Sio_2.\,5H_2O$ closely approaching to our mineral has been mentioned in literature under the name of «hydrotalc». It has been adopted on the basis of Longchambon's ([7]) statements. However, both formally and from its essence, this term is not fit to denote the sepiolite variety called by the author «β sepiolite».

** In the majority of the formulae suggested, the coefficients with H_2O (combined H_2O+ and H_2O-) are taken equal to 6. It is to be noted that this value is an average one; as a matter of fact, it varies between 5 and 8.

*** It stands to reason that to the hydrosyalite molecules correspond their really existing ferruginous and chromic analogues, as well as there exist Fe″, Ni, Mn which are the analogues of sepiolite ([8]).

**** In this connexion it is important to note that the constitution of glauconite minerals should be explained by an equivalent substitution $(Fe'', Al)_2O_3$ with 3(Mn, Fe″, Ca, K_2, Na_2 and Li_2) O respectively in molecules of the type: $(Fe, Al_2O_3 \cdot 2SiO_2.nH_2O$, $Fe'', Al)_2O_3.\,3SiO_2.\,nH_2O$, and with those intermediate with regard to their silica-content.

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METEOROLOGY

METEOROLOGICAL CONDITIONS IN RELATION TO AVALANCHES AT KHIBINY

By A. P. PAVLOV

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Avalanches depend on numerous causes of an extremely varied nature. These causes, however, may be arranged in three main groups as follows:

1) The character of the mountain slope, down which the avalanche slides.
2) The volume and structure of the snow.
3) The meteorological conditions.

The significance of the last group, i. e. of the meteorological conditions, for avalanches is exceptionally great. Suffice it to say that the division of avalanches into dry ones and wet ones is essentially based on temperature, that is, a meteorological factor. The changes proceeding on the surface of and inside the mass of snow are of a complex nature and to a considerable extent are the result of one or another of the meteorological conditions. Furthermore, neither the slope nor the snow vary with the locality to such an extent as do the meteorological factors which exhibit a wide range of variations in different regions and even within one and the same region and, therefore, lead to avalanches of greatly varying nature.

For this reason the large experience gained in combatting avalanches in the Alps cannot be fully utilized in Khibiny, since the meteorological conditions of these two regions differ widely.

The main cause of avalanches in the Alps is heavy snowfall. The air currents from the Mediterranean and the Atlantic Ocean carry a large amount of moisture and in the winter when they reach the heights of the Alps, the slopes of which are covered with snow, the moisture becomes intensively condensed and as a result the layer of snow is in the course of but one month topped by a new layer five and even seven meters thick.

„In 1931, measurements taken every hour at Vallis showed an increase of 20 cm in the thickness of the snow per hour»(1). Such an exceptionally heavy snowfall inevitably leads to avalanches.

The Alps are noted for a number of other meteorological conditions besides heavy snowfall, such as thawing in the winter, föhn winds and rain on the snow-covered slopes. For all these reasons avalanches in the Alps hold a singular place. Naturally, the conditions making for avalanches determine the methods of combating such avalanches.

The Khibiny mountain massif, lying beyond the Arctic Circle, naturally has its own meteorological conditions. The annual amount of precipitation

at Khibiny, which is close to the sea and particularly to the Gulfstream, is fairly high; it varies between 700 and 800 mm and sometimes in the central part of the mountain range even totals 1000 mm. Such an amount of precipitation for so high a latitude is undoubtedly considerable. Snowfall notwithstanding the seven months of winter accounts for less than one half of the precipitation, viz., for 300 mm or 350 mm at the outside. The snowfall, of which there are altogether about 160 days, is rather weak, the daily maximum averaging between no more than 6 or 7 mm. The increase in the thickness of the snow in the course of one day never exceeds 20 cm, and even such an increase is rare. Snow falling so scantily here could not naturally cause big avalanches. Observation has shown that snowfall accounts for no more than 7 or 8% of the avalanches at Khibiny, when volume is in most of the cases below 100 cubic meters.

Temperature is a factor in avalanches because while passing through zero point its effect is either to thaw or congeal the snow. This transition of water from one phase to another is a most important meteorological factor. Thawing in the winter followed by cold weather leads to the formation of a snow crust at the surface. As long as there is no fresh snowfall this crust serves a good purpose in binding the snow on the mountain slopes. Its rôle is essentially changed, however, after it has become covered with a fresh layer of snow. Then it presents a fairly smooth surface, for the upper layer of sharply different density to slide on it. The lack of sufficient cohesion between these two layers leads to avalanches.

Thawing in the winter is more likely to occur in the mountains than on the valleys, for thawing in the valleys may be caused solely by warm air currents whereas in the mountains it may also be caused by temperature inversion and föhn.

There is hardly any thawing at Khibiny between December and the end of March. During an observation period of four years there were no more than six days when the temperature was above zero at this time of the year. The reason seems to lie in the far northern position of the massif which is reached by the warm air currents when they are sufficiently cooled. On the other hand, the low elevation of the Khibiny accounts for the fact that the föhn in the winter does not, as a rule, raise the temperature to zero. Temperature inversions at Khibiny are due to the lowering of the temperature at the base and not to its rise at the top of the mountain as is the case in the mountain regions lying in a more southerly direction. However, in the first half of winter, particularly during the period when the snow is beginning to cover the ground, cases of thawing are frequent at Khibiny. The dropping of the temperature to zero and below zero continues during a long period of time, in the course of which zero is repeatedly reached, and as a result one or even several thick layers of snow crust are formed. In addition the slight oscillations above and below zero lead to the formation of an ice-crust.

We have had many occasions to observe a smooth crust of ice forming on the upper part of the mountain slopes before the ground is covered with snow. A more ideal surface for the sliding of the snow could hardly be imagined. It is because of the snow and ice crusts that avalanches at Khibiny occur mostly in the first half of winter. In the course of time, owing to the process of recrystallization within the snow cover, the snow and ice crusts are gradually destroyed and their significance is at any rate considerably reduced.

In the winter the general circulation of air at the Kola peninsula and particularly at Khibiny greatly depends on the Iceland minimum pressure, whose eastern branch runs north of the peninsula in the summer, shifting southward onto the peninsula in the winter. This branch constitutes the track frequently swept by cyclones. The cyclons' change of track in the direction

the continent accounts for the minimum pressure on the Kola peninsula falling out in the winter. The greater cyclonic activity in the winter is marked by frequent snowfalls and stronger winds accompanied by frequent snowstorms. This is still aggravated by the complex configuration of the mountains. That is why snowstorms are to be considered as something normal for the Khibiny in the winter, particularly in the upper part of their slopes.

Observations made at the Khibiny meteorological station in the course of five years have shown that two thirds of all the days between November and the end of April are marked by snowstorms and that the total number of such days reaches 150 in the course of one year.

At Khibiny there is not a single area where the thickness of the snow corresponds to the fall of snow. This is the effect of the wind which drives the snow from the open spaces to quiet and secluded ones, such as hollows or cirques; here snowdrifts are formed and avalanches of great force involving tens and hundreds of thousands of cubic meters of snow occur. The thickness of the snow layer in these recesses is three to four times the normal. The wind, besides storing up enormous masses of snow in the recesses, also forms cornices which, when breaking down, often start an avalanche. It should be noted that this irregular distribution of snow has another very important effect. As is known, the snow as a result of a number of causes is constantly settling. Add to this that on the mountain slopes it is slowly sliding downward, like a glacier. The intensity of these processes, particularly of the settling, is closely related to the thickness of the snow. Therefore, the greater the irregularity in the distribution of the snow, the greater the difference between the indicated processes operating in the adjacent areas. This, in turn, leads to the unequal distribution of the forces of inner tension and, consequently, facilitates the first movement of the mass of snow.

At long last we should note the part played by winds in forming special snow crusts which have the same relation to avalanches as have the crusts formed by the variations of temperature.

The density of those crusts according to my observation amount to 0.43 and the thickness of some tens of centimeter.

In the second half of winter, when the snow is thicker than ever, the layer of hoarfrost is very thick and snowstorms continue with unabated force, a sharp decline is to be noted in the number of avalanches. This is because the snow blown by the wind fills the hollows by the middle of winter and with that a rather even slope is created. Further on the distribution on the mountain slides of the snow by the wind proceeds more evenly. The slopes are no longer overloaded with snow as they are in the first half of winter. Consequently, the conditions that formerly led to avalanches to a considerable extent disappear.

Avalanches caused by snowstorms occur in particular places. It is therefore comparatively easier to combat these avalanches than those caused by heavy precipitation, since the latter endanger most of the sections of the mountain slope.

The greatest number of avalanches occur when the velocity of the wind ranges between 7 and 10 m per second (49%). When the velocity of the wind varies between 5 and 12 m per second the number of avalanches reaches 70%. However, it would be wrong to look for a direct connexion between avalanches and velocity of wind. The velocity of the wind being the same, the results may, however, differ depending on the condition and volume of the snow on the slopes. Hence, it is not the wind but the snowstorm that serves as a meteorological factor of decisive importance for the phenomena of avalanches in Khibiny. This conclusion relates to dry avalanches which occur in the winter when the temperature is below zero.

Quite different are the conditions of wet avalanches, i. e. avalanches of wet snow.

Wet avalanches are usually smaller in volume, develop less speed in sliding and have a shorter track. However, under the conditions prevailing at Khibiny, some of these avalanches, as for instance, those carrying rock, are as powerful as the dry avalanches.

It is quite clear that temperature is the principal meteorological factor causing wet avalanches. The temperature rising to zero has as its effect the thawing of the snow, consequently, increase in the density of the snow and the formation of a surface facilitating sliding, that is, it creates all the conditions that immediately lead to an avalanche.

The bulk of the heat that causes the thawing of the snow and consequently avalanches is derived from warm masses of air. Over 80% of the wet avalanches occur when cloudiness exceeds 50%, while 69% of the avalanches occur when there is 100% cloudiness. The proportion of the wet avalanches is about the same when the wind constituent is directed toward the south. Hence, the part immediately played by the sun in causing avalanches is fairly insignificant.

Sun radiation has a great effect in causing a slight sliding of the upper layer of snow and as a result the daily downward movement of the snow is clearly evident.

Kola-Base.
Academy of Sciences of the USSR.

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HYDROBIOLOGY

ORGANIC MATTER IN WATER OF CERTAIN SEAS

By V. G. DATZKO

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Attempts to isolate individual organic compounds from sea water have not been successful as yet on account of their low concentration and the presence of high amounts of salts in the sea. One of the possible methods for ascertaining organic matter available in sea water is to estimate the amounts of carbon and nitrogen held in solution.

This method is also the basis of the present work, which has for object to get an idea of the amount and the quality of organic matter in the water of certain seas. The estimation of the organic carbon and nitrogen dissolved in the respective waters was made according to Krogh and Keys (1). But the thallium sulphate by whose means these authors precipitated chlorine from the sea water in determining its content of organic carbon was replaced by the sulphate of silver, and in determining the content of nitrogen the colorimetric instead of the volumetric method (Nessler reaction) was used for the estimation of ammonium in the distillate.

The analysis was made in water samples preserved by means of corrosive sublimate. Organic carbon was estimated in the samples treated with silver sulphate; organic nitrogen, in the samples of natural sea water after its ammonium has been drawn out at 60°C.

The error involved in the method of testing is ± 0.2 mg/l for carbon, and $\pm$ 0.02 mg/l for nitrogen. The results are summarized in Table 1.

The conclusions to be drawn from these data are as follows.

The content of carbon and nitrogen in the Sea of Azov and the Caspian is higher than in other seas investigated. The water in the Caspian Sea is much more abundantly stored with organic carbon compared to the Sea of Azov but it is poorer in nitrogen. It would seem that the conditions prevailing in the Caspian Sea favour the accumulation of stable organic substances decreased in nitrogen which appear to be chiefly of allochthonous nature. The reason for their storing up here is the closeness of the basin, the profuse evaporation and the inflow of organic matter conveyed by the drainage. The gulf of Karabugaz may serve as a very representative instance of accumulation of organic matter in water. According to Skopintzev (2), the acidification value for the superficial water of the gulf is 8.5 times higher compared to the open part of the Caspian Sea and the ratio of oxidability in the neutral and the alkaline medium is near to that for sea water. This has to be taken to mean that this gulf and the open sea are much alike as regards the composition of their organic matter. And it seems, therefore, only natural to ascribe

Table 1

Water basin	Coordination of sampling station	Date of sampling	Depth in m	Level	Carbon in mg/l	Average in mg/l	Nitrogen in mg/l	Average in mg/l	C/N ratio
Greenland Sea	79°58′N 03°40′E	9.IX.1933	1000	0	—	—	0.21		
				25	2.1	2.1±0,2	—	0.22±0.02	9.5
				750	2.0		0.23		
White Sea	65°52′N 37°02′E	19.IV.1934	120	25	2.5	—	—		
				50		2.6±0.2	0.30	0.31±0.02	8.3
				100	2.6		9.32		
Black Sea	44°16′N 36°30′E	26.IX.1937	About 1500	25	2.4		0.22		
				300	2.3	2.4±0.2	0.27	0.25±0.02	9.6
Sea of Azov	46°03′7″N 36°44′E	24.IX.1937	11	0	3.0		0.61		
				10	3.2	3.3±0.2	0.58	0.62±0.02	5.3
	45°58′3″N 37°45′52″E	20.IX.1937	8.8	0	3.7				
							0.67		
Caspian Sea South	39°00′N 50°42′E	19.II.1934	948	25	5.9		0.49	0.49±0.02	11.4
				400	5.2	5.6±0.2	0.48		
				940	5.6		0·50		
Centrum	42°07′N 48°56′E	7.IX.1936	586	400	5.6	5.6±0·2	0.48	0.48±0.02	11.7

the allochthonous origin to the bulk of organic matter in the gulf of Karabugaz. Similar way of storing up organic matter is also possible in the Caspian Sea.

The Sea of Azov however is a basin of running water. Its water exchange with the Black Sea prevents such an abundant accumulation of organic matter as is observed in the water of the Caspian Sea. Very different is also the character of the organic matter occuring here, as it may be inferred from the C/N ratio. The low quotient of C/N for the Sea of Azov ([5],[3]) speaks of sufficient «freshness» of organic matter whose considerable part has not yet decreased in nitrogen appreciably during the process of disintegration.

The content of organic carbon and nitrogen in the water of the Greenland and the Black Sea approaches to that in the Atlantic. In the latter the average content of organic carbon is, according to Krogh ([3]), 2.35±0.09 mg/l, and that of nitrogen, 0.244±0.01 mg/l. The quotient of C/N is nearly 10. However, no water samples were taken in the Black Sea below a depth of 300 m and the ratio of C to N may possibly change if we descend deeper.

The water of the White Sea is higher in both organic carbon and nitrogen than are the ocean waters and its quotient of C/N is somewhat lower. The reason seems to lie in the influence of the drainage and in the biological processes having place in the basin.

The vertical distribution of organic carbon and nitrogen is rather even in the waters investigated with the single exception of the Black Sea where the amount of organic nitrogen grows with the depth.

Since the organic carbon was estimated in the samples treated with the sulphate of silver while the samples of organic nitrogen were not treated at all, the data on carbon refer to the dissolved organic carbon and the data on nitrogen to its total content in water.

When the samples for nitrogen were treated with the sulphate of silver the results were as shown in Table 2.

For all the waters tried, except the Sea of Azov and the superficial layer of the Caspian Sea, the proportion of deposited nitrogen is small, not exceeding the error, and the ratio of C to N does not change appreciably. In the Sea of Azov the quotient of C/N was found to increase from 5.3 to 8.2.

Table 2

Water basin	Level in meter	Organic nitrogen in untreated sample mg/l	Organic nitrogen in treated sample mg/l	% of precipitated N	Organic carbon in the same sample mg/l	C/N ratio
Sea of Azov	0	0.67	0.45	32.8	3.7	8.2
Southern Caspian . .	25	0.49	0.37	23.5	5.9	15.9
	400	0.48	0.48	0.0	5.2	10.8
Centrum Caspian . .	400	0.47	0.45	6.2	5.6	12.4
Black Sea	25	0.22	0.21	4.5	2.4	10.9
White Sea	50	0.30	0.29	3.3	2.6	9.0

It is very likely that the chief part of the deposited nitrogen ows its origin to the suspensions of organic matter in the sea water (plankton, detritus, colloidal substances).

If we take it for granted that the water samples from the Sea of Azov precipitate 1/3 of their organic carbon when treated with silver sulphate, as it is the case with nitrogen, then we have to increase the average total of organic carbon for the Azov Sea up to 4.4 mg/l. And in turn the amount of carbon in the superficial layers of the Caspian Sea must be raised to 7.4 mg/l while its average content in this sea, to 6.0 mg/l.

Amount of Organic Matter in Terms of Protein and Carbohydrates

While expressing the results obtained in terms of proteins and carbohydrates, the average content of carbon in the latter was taken equal to 52 and 40% respectively and the content of nitrogen in the proteins was supposed to be equal to 16%.

In recalculation the average data on carbon and nitrogen referred to in Table 1 were made use of. The data on carbon referring to the Sea of Azov and the Caspian Sea were corrected for the precipitation by silver sulphate during the treatment of the samples; these data are 4.7 and 6.0 mg/l, respectively. The results of calculation are presented in Table 3.

Table 3

Water basin	Protein mg/l	Carbohydrates mg/l	Total of carbohydrates and protein, mg/l
Caspian Sea	3.1	11.0	14.1
Sea of Azov	3.9	6.0	9.9
White Sea .	1.9	4.0	5.9
Black Sea .	1.6	4.0	5.6
Greenland Sea	1.4	3.5	4.9

Greenland, Black and White Sea waters approach to the Atlantic as regards the quantitative and qualitative composition of their organic matter. According to Krogh [3] a liter of Altantic water contains 1.5 mg of protein and 3.9 mg of carbohydrates.

The Sea of Azov and the Caspian Sea have their content of organic matter very near to that of some lakes. Krogh [4] has found the water of the Danish lakes to contain 3.3 mg of proteins and 5.5 mg of carbohydrates per liter.

The content of organic matter in the Sea of Azov is somewhat higher than it is in the Danish lakes. The Caspian Sea is nearer to the lakes of Wisconsin (U. S. A.), the amount of organic matter in the water of the lake Mendota is 14.57 mg per liter (3.67 mg/l of proteins and 10.22 mg/l of carbohydrates) ([5]).

The water of the Caspian Sea is so much alike that of the lake Mendota with regard to the quantity and quality of its organic matter that it is tempting to make use of the works by Peterson, Fred and Domogalla for throwing light upon the quantitative composition of nitrogen containing substances in the Caspian Sea. The composition of these substances reported by the above authors in the water from the lake Mendota may possibly apply quantitively to the organic matter of the Caspian Sea.

All-Union Institute
of Sea Fisheries and Oceanography.

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GENETIK

EINFLUSS DES COLCHICINS AUF DIE SPERMATOGENIALMITOSEN BEI DEN ORTHOPTEREN

Von IWAN SOKOLOW

(Vorgelegt von N. I. Vavilov, Mitglied der Akademie, d. 19. V. 1939)

Es wurden im Juni 1938 einige Versuche über den Einfluss des Colchicins auf die Spermatogenialmitosen bei den Heuschrecken (*Chorthippus* sp. div.) angestellt, welche, trotz ihres vorläufigen Charakters, immerhin gewisse interessante Ergebnisse geliefert haben.

Eine 0.07% Lösung des Colchicins wurde mittels einer feinen, mit einem Gummiballon verbundenen Glasnadel in das Abdomen der Heuschrecken eingeführt. Es wurden junge männliche Tiere (im 2. oder 3. Stadium) behandelt, deren Gonaden alsdann nach 24 Stunden mit Navaschin's Gemisch fixiert wurden. Die Schnitte wurden mit Eisenhaematoxylin nach Heidenhain gefärbt.

Nach Verlauf von 24 Stunden nach der Einführung der Colchicinlösung äussert sich deren Wirkung darin, dass bei den sich teilenden Spermatogonien (sowie den die Kodenschläuche umgebenden Bindegewebszellen) keinerlei regelrechte Metaphasen zu beobachten sind. Infolge der Inaktivierung oder Entwicklungshemmung des Spindelapparates unterbleibt die Wirkung des orientierenden Mechanismus, der an die Zentrosomen und Zentromeren (kinetische Einschnürungen) gebunden ist; und das führt zu einer völlig regellosen Lagerung der Chromosomen in der Zelle.

Gleichzeitig findet eine starke Veränderung der äusseren Gestalt der Chromosomen statt. Die 3 Paar grosse Chromosomen von *Chorthippus*, die normalerweise V-förmig mit langen, ungleich grossen Armen erscheinen (Fig. 1,2), verkürzen sich über die Grenzen der für die spermatogonialen Metaphasen charakteristischen Norm. Hand in Hand damit erfolgt ein allmähliches Auseinanderklappen ihrer Arme. Wenn letztere normalerweise zusammen einen spitzen Winkel bilden, so wird dieser zunächst gerade, dann stumpf (Fig. 3), bis schliesslich die beiden Chromosomenarme in einer geraden Linie zu liegen kommen (Fig. 4). Verschiedene Momente dieses Vorganges können nicht nur an Chromosomen verschiedener, in derselben Spermatocyste gelegenen Spermatogonien, sondern auch an einzelnen Chromosomen ein und derselben Zelle beobachtet werden. Die allgemeine Verkürzung ist dermassen stark, dass in extremen Fällen die Chromosomenlänge mehr als auf das Doppelte gegenüber der Norm herabgesetzt wird (vergl. Fig. 1 mit Fig. 6, 8). Gleichzeitig nimmt die Breite der Chromosomenarme entsprechend zu. Ein besonderes Interesse bietet dabei das scharfe Hervortreten der kinetischen Einschnürungen dar, da das Chromosom an dieser Stelle plötzlich stark eingeengt erscheint und die kinetische Einschnürung die

Gestalt einer schmalen und relativ langen Brücke erhält (Fig. 5, 6, 9), während sie sonst das Aussehen einer einfachen Ringfurche am Chromosomenkörper oder einer kurzen achromatischen Unterbrechung hat (Fig. 1, 2).

Die übrigen 5 Paare kleiner, stabförmiger Autosomen mit terminaler Ansatzstelle der Spindelfaser erleiden eine ähnliche starke Verkürzung. Ihr Proximalende ist gewöhnlich leicht verschmälert und meist mit einem kleinen, zugespitzten Vorsprung versehen (Fig. 15, 16). Unter der Einwirkung des Colchicins wird dieser letztere deutlicher abgesondert und erscheint bald abgestumpft, bald zugespitzt (Fig. 17, 18, 19). Beim allerkleinsten Chromosom erreicht ein derartiger Vorsprung öfters eine Länge, welche der Länge der Chromatiden selbst, die hier eine fast kugelige Gestalt haben, gleichkommt (Fig. 21, 22).

Zweiarmige (Fig. 1—14) und einarmige (Fig. 15—22) Chromosomen aus normalen (Fig. 1, 2, 15 und 16) und aus mit Colchicin behandelten (Fig. 3—14 und 17—22) Spermatogonien von *Chorthippus* sp.

Bei gewöhnlicher Differenzierung des Präparats erscheinen sowohl die kinetischen Einschnürungen der zweischenkeligen, als auch die Proximalvorsprünge der stabförmigen Chromosomen grau oder dunkelgrau gefärbt, während die Chromatiden eine tief schwarze Färbung zeigen. Da bei sämtlichen Zellen die Bildung der achromatischen Figur unterbleibt und keinerlei an die Chromosomen gebundenen Spindelfasern zu sehen sind, so kann über die Art und Weise der Anheftung der Spindelfasern nichts gesagt werden. Irgend welche Anzeichen von «Leitkörperchen», die gewöhnlich als intensiv sich färbende Körnchen beschrieben werden [Trankowsky (7), Schrader (6), Ellenhorn (1) u. a.], wurden nicht beobachtet. Gegenüber den Angaben von White (8), welcher bei den stabförmigen Chromosomen von *Locusta migratoria* den zweiten Arm in der Form eines stark färbbaren Köpfchens, das durch die achromatische kinetische Einschnürung vom übrigen Chromosomenkörper abgetrennt wird, beschreibt,—konnten bei ebensolchen Chromosomen von *Chorthippus*, trotz des eifrigen Suchens, keinerlei Spuren eines zweiten Armes nachgewiesen werden. Man bekommt den Eindruck, dass wir hier mit echten einarmigen Chromosomen zu tun haben deren Existenz, wie bekannt, von den meisten Autoren angezweifelt wird [Geitler (2)],—wobei der Proximalvorsprung in toto als Homologen der kinetischen Einschnürung der zweiarmigen Chromosomen anzusehen ist. Um ein endgültiges Urteil über diese Frage zu fällen, wären aber noch andere Untersuchungsmethoden als die hier erwähnten zu erproben.

Auf ein und demselben Präparat, nicht selten auch innerhalb derselben Spermatocyste, kann man die verschiedensten Stadien der Chromosomenteilung vorfinden und somit Schritt für Schritt den Übergang von diploiden zu den tetraploiden Spermatogonien verfolgen. Auf einem Stadium, das der frühen Metaphase entspricht, bleibt die kinetische Einschnürung der zweiarmigen Chromosomen, im Gegensatz zu normalen Verhältnissen, noch ungeteilt, während die Chromosomen selbtst nicht nur aus zwei Chromatiden bestehen, sondern auch die Chromatiden längsgespalten sind (Fig. 7). Diese Längspaltung der Chromatiden wird mit genügender Klarheit auch bei nicht behandelten Chromosomen beobachtet. Die erste Veränderung besteht darin, dass die Chromatiden mit ihren freien Enden sich gegenseitig abzustossen beginnen, wodurch das ganze Chromosom eine sonst ungewöhnliche, aber für die mit Colchicin behandelten Zellen recht charakteristische X-förmige Gestalt annimmt (Fig. 7—9). Erst später geschieht die Längteilung der kinetischen Einschnürung, wobei dieser Vorgang nicht simultan erfolgt, sondern an deren Enden beginnt und zwar zunächst an dem dem längeren Arm zugekehrten Ende (Fig. 10,11). Kurz vor Abschluss der Teilung bleibt die kinetische Einschnürung noch eine Zeitlang in ihrem mittleren Teil ungespalten, wodurch das Bild eines nicht ganz regelrechten Kreuzes entsteht (Fig. 12). Im nächsten Moment wird die Teilung vollendet, und die Spermatogonien werden tetraploid. Die eben entstandenen Tochterchromosomen bleiben zunächst in der Zelle zu engen Paaren angeordnet liegen (Fig. 13), dann aber entfernen sich immer mehr und mehr voneinander. Aber auch jetzt bewahren sie noch lange ihre parallele Orientierung (Fig. 14). Es sei noch erwähnt, dass auch auf dem letzt geschilderten Stadium nicht selten der dorsiventrale Bau der neuentstandenen Chromosomen erhalten bleibt, insofern als die kinetische Einschnürung nicht mit der Hauptachse des Chromosoms zusammenfällt, sondern mit derjenigen Linie ihrer cylindrischen Oberfläche, die in der Prophase dem Längspalt zugekehrt war (Fig. 13, 14).

Trotz des vorläufigen Charakters der vorliegenden Beobachtungen erlauben sie immerhin den Schluss zu ziehen, dass die Reaktion der tierischen Zellen auf die Einwirkung des Colchicins und eine solche der pflanzlichen Zellen grundsätzlich ein und derselbe ist. Besonders gut stimmen unsere Resultate mit den Beobachtungen von Levan ([3], [4]) [s. auch O'Mara ([5])] an den Mitosen der Wurzelspitzen und der ersten Teilung des Pollens bei gewissen *Allium*-Arten überein, wo ganz ähnliche Veränderungen sowie dieselben charakteristischen Teilungstadien der Chromosomen, wie bei den Spermatogonien der Heuschrecken, beobachtet wurden. Somit äussert sich auch hier die selektive Wirkung des Colchicins, die zu einer Inaktivierung des achromatischen Apparates führt. Es darf wohl angenommen werden, dass die Einwirkung des Colchicins auf die Spindelansatzregion mit einer Verzögerung ihrer Teilung im Zusammenhang steht, was sich u. a. speziell in der kreuzförmigen Gestalt der zweiarmigen Chromosomen kundgibt, die normalerweise nicht vorkommt.

Laboratorium für Genetik
und experimentelle Zoologie der
Staats-Universität.
Leningrad.

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PHYTOPATHOLOGY

BIOCHEMICAL CHANGES IN OATS AFFECTED WITH THE VIRUS DISEASE «ZAKUKLIVANIE»

By V. L. RISCHKOV, M. N. VOROBIEVA and E. P. GROMYKO

(Communicated by V. L. Komarov, Member of the Academy, 13. VII. 1939)

The virus nature of the disease in question has been established by the work of Sukhov and Vovk, who have also discovered its carrier and described in detail its anatomo-morphological symptoms. The present investigation was started with the aim to characterize the disease in its biochemical aspect.

Many authors have been concerned with the study of the nitrogen and the carbohydrate metabolism in plants attacked by virus diseases. The result of their work is the statement that the account of carbohydrates is reduced in plants affected with mosaic. Any important change in the content of total nitrogen is not usual in that case as well as in the case of yellows when the above-ground parts of the plants increase in carbohydrates. As to the protein nitrogen, its content was found to rise in response to several virus diseases, say the tobacco mosaic, but this is not a general law and there are many more cases of virus infection where no change whatever or even a decrease in the content of protein nitrogen was noticed. For a more detailed information on this subject the reader is referred to the work by Rischkov.

It was claimed in the previous reports (by Sukhov and Vovk, Rischkov and Gromyko) that the amount of both total and protein nitrogen goes up under the influence of «Zakuklivanie», but the conclusion was reached by analyzing entire plants and this is not a proper method to characterize the condition of the metabolism, since the sound plants have their stem system normally developed while in the dwarfs it is very weak and consists largely of leaves. Now we have proceeded therefore to the estimation of nitrogen in the leaves of sound and diseased oats. The tests were run with the leaves of both dwarfs and mosaic plants. In the case of oats these two kinds are only different forms of the same disease called «Zakuklivanie». Nitrogen was estimated according to Kjeldahl. The results of the analysis are summarized in Table 1.

Table 1

Nitrogen Content in the Leaves of a Sound and a Diseased Oat, Variety Lokhovsky (in % of dry weight)

Material	Total N	Protein N	Non-protein N
Sound	2.9496	2.5223	0.4107
»	2.8672	2.5465	0.3325
Mosaic	2.9567	2.4097	0.5826
»	2.9647	2.3965	0.6460
Dwarfs	3.0558	2.1265	0.9393
»	3.1481	2.1664	0.9541

From Table 1 it is evident that the dwarfs increase in total and non-protein nitrogen, while they show a slight decrease in protein nitrogen. In sum, no significant change of nitrogen content is observed in the leaves.

The carbohydrate content was estimated according to Bertrand. The estimation involved the reducing as well as the non-reducing sugars and the starch which were divided according to the methods described by Kiesel. The data obtained are presented in Table 2.

Table 2

Carbohydrate Content in the Leaves of a Sound and a Diseased Oat (in % of dry weight, glucose units)

Material	Sugars		Starch	Total
	Reducing	Non-reducing		
Sound	9.625		1.013	14.255*
»	9.464	3.532	1.347	
Dwarfs	12.199	6.319	2.879	20.438
»	11.935	4.944	2.701	

Such increase in C/N is a characteristic of the yellows. And there are still other indices, viz.: the injury of the phloem, and the transmission of the infection by the insects, which suggest this type of disease for «Zakuklivanie». We meet here also with the autholysis and prolification of flowers, which are the symptoms of many of the yellows, say of stolbur in *Solanaceae* and are not observed to attend the mosaics. But along with this there are some other symptoms which are characteristic of the mosaics; such are the mosaic pattern in the colouring and an abundant accumulation of protein crystals in the cells. Particular interest belongs therefore to the «Zakuklivanie» of oats on account of its intermediate position between the yellows and the mosaic, whose symptoms are united in it.

The fact that the parasitic nucleoproteids were found to play the rôle of the causal agent in a number of virus diseases directs our special attention to the phosphorus metabolism in the plants attacked by the virus. Unfortunately, no data on this subject are available in the literature. The estimation of P in the oat leaves was made according to the colorimetric method of Denezhe-Levitzky (quoted from Gedroiz) in various fractions: ether-alcohol extract, fraction soluble in 9.95 *N* HCl and the residue. Total phosphorus was determined separately and not by way of summation.

Table 3

Content of P_2O_5 in the Leaves of a Sound and Diseased Oat, Variety Lokhovsky (in % of dry weight)

Material	Total P_2O_5	P_2O_5 ether-alcohol extract	P_2O_5 soluble in 0.05 *N* HCl	P_2O_5 residue	P_2O_5 in 3 fractions
Sound	0.0989	0.0106	0.0592	0.0291	0.0990
»	0.0992	0.0102	0.0568	0.0322	—
Mosaic	0.0821	0.0040	0.0606	0.0329	0.0970
»	0.0831	0.0047	0.0616	0.0323	—
Dwarfs	0.1536	0.0045	0.1016	—	—
»	0.1659	0.0049	0.0989	0.0337	0.1386

* Obtained by summing up the average data.

As seen from Table 3, the phosphorus metabolism is liable to change sharply under the influence of „Zakuklivanie".

The diseased plants decrease strongly in the lipoid form of the phosphorus, while they increase in the form soluble in a weak HCl and this is especially true of dwarfs. The residual phosphorus does not change in amount.

The latter is largely the phosphorus of insoluble nucleoproteids, which do not appear to be affected quantitatively by the disease. The form soluble in weak concentrations of HCl is a complex composition. Besides the mineral phosphorus, it contains the organic one, partly from water soluble proteins. Virus nucleoproteid, if responsible for the disease, may possibly occur among the latter. Of a more definite character is the phosphorus soluble in ether and alcohol, this is the phosphorus of lipoids. The reason for its sharp decrease in diseased plants seems to lie in the reduction and degeneration of plastids, which is observed in plants attacked by „Zakuklivanie". Vorobieva has found the abutilon also to decrease in lipoid phosphorus considerably under the influence of infectious chlorosis.

Conclusions

1. The leaves of oats do not show any significant change of nitrogen content in response to the infection studied. The dwarfs increase to a certain extent in total nitrogen and decrease in protein nitrogen.
2. The effect of the disease is to increase the content of reducing as well as non-reducing sugars and of starch.
3. Most of the symptoms and among their number the ratio of carbohydrates to nitrogen point to the fact that this disease of oats should be classed with the yellows, but is is also attended by some typical symptoms of mosaic.
4. The phosphorus metabolism is greatly affected by the disease. The leaves of the sick plants decrease in the lipoid phosphorus, increase in the phosphorus combined in compounds soluble in 0.05 *N* HCl and show no change in the remainder.
5. The decrease in the lipoid form of phosphorus appears to be related to the reduction and disintegration of plastids which is observed in the diseased plants.

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ZOOLOGY

LARVA OF *SENOTAINIA TRIGUSPIS* MEIG. CAUSING HEAVY LOSSES OF BEES

By A. K. BOYKO

(Communicated by I. I. Schmalhausen, Member of the Academy, 5. V. 1939)

Among epizootic diseases of adult honey bees there is a group of widely spread diseases to which beekeepers give the collective name „summer loss of bees", characterized by sudden dying out of great numbers of flying bees during the busiest season of the colonies. Attempts of beekeepers to refer outbreaks of such diseases in some cases to poisonous nectareal plants, visited by bees at that time, are not borne out by evidence. Thus, in the Ukrainian SSR are particularly frequent cases of „summer loss of bees" concurring with the blooming of the mint *Thymus serpyllum*, whose nectar is believed to be in many places „injurious", although in other places the visiting of this splendid nectar bearing plant does not result in any injurious effect on the bees.

The true etiological factors for the whole group of such diseases have long remained unknown. Only quite recently it has been ascertained that the mass destruction among bees in the summer time is due in some cases to bacterial septic diseases (C. E. Burnside, 1929, A. K. Boyko, 1935). But the group of bacterial diseases is far from including all the cases of similar epizootic diseases of bees, and most of them are apparently caused by other agents.

In literature are contained data on larvae of various representatives of *Diptera* parasitizing in the internal organs of the bees. Thus, in South Africa the larvae of the fly *Tachine Rondaniocestras apivorus* Villeneuve parasitize in the intestine of bees (Scaife, 1926). In France cases are reported of larvae of the fly *Myopis Angellozi* to parasitize in the thorax of bees (Segui). The parasitizing of such larvae is said to cause no material damage to beekeeping. Borgmeier described in 1935 the fly *Melaloncha Ronnai* Borg. from the family *Phoridae* whose larvae live as parasites in the thorax of bees, killing a great number of bees in the summer time, and thus causing great damage to beekeeping in Brazil.

In the USSR larvae of certain flies were for the first time discovered in the thorax of bees in 1926 by L. I. Perepelova; later on in 1931, V. V. Alpatov found larvae of flies from the family *Conopidae* in the intestine of bees sent from the town of Stary Krym. The apiarist Gura reported in 1936 that in the Olkhovat district of the Voronezh province during the period of June—August some larvae are often discovered in the thorax of bees. Lastly, in 1938 information was obtained from P. P. Myshkin that in Kirghizia the intestine of bees are infested with larvae of the fly *Physocephala villata* F. fam. *Conopidae*.

All these communications, although coming from various parts of the USSR, and based on incomplete evidence not excluding the possibility of postmortal infection with larvae of various flies, still lead to the suggestion that certain species of flies in the USSR apparently play a definite part in the etiology of the „summer loss of bees". The above communications did not imply, however, that the diseases were epizootic or that they caused direct losses to apiculture.

Our investigations were undertaken in 1937, when in the apiaries of the Minovsk and adjoining villages of the Poltava district during the period of June 8—20 there was a violent outbreak of the disease, causing a high death rate in colonies of flying bees. In the thorax of diseased and dying bees there was always discovered a single living larva of some fly. There have been found no agents of other known diseases. Similar outbreaks of the „summer loss of bees" in this locality have been known to beekeepers ever so long and their occurrence always coincide with the blooming of the mint *Thymus s.*, as was the case in 1937. The same year such larvae of flies were discovered in the thorax of dead bees, received from 2 districts of the Donetz province, one district of the Dnepropetrovsk province and 4 districts of the Kharkov province. Most of the data collected from apiaries which had sent this material, testified to the heavy death rate among bees and were connected with their visiting the mint *Thymus s.*

In 1938 we had occasion to watch similar epizootic diseases in several apiaries at the Ostersk district of the Chernigov province. They resulted in a sharp drop in the number of flying bees of the stock within the period of 5—8 days at the end of July. A great percentage of bees of the weak colonies of those apiaries were found to contain larvae of flies.

An identical disease was registered in 1938 in the apiaries of V. Bagachansk district of the Poltava province. But a particularly violent outbreak of disease was reported in 1938 from the apiaries of the Kremenchug district of the Poltava province, where 50% of all the colonies and 100% of colonies which have been gathering nectar from *Thymus serpyllum* were affected by this disease. Owing to the loss of the greater part of the flying bees, these apiaries lost altogether the abundant honeyflow from *Thymus*.

These data collected by us testify to that many cases of „summer loss of bees" are due to larvae of flies parasitizing in the body of the bee.

The size of larvae found in the thorax of bees varied from 1 to 6—7 mm and even up to 8 mm in length depending upon their age. The thoracic muscles of the bees were in such cases partly or wholly destroyed by the larvae. The larvae concerned possessed 2 pairs of well developed mouth hooks. The body surface of the larvae is smooth with segmentation well pronounced. The posterior pair of stigmata is lying in a sac-like cavity. The colour of young larvae is pearly-white, taking on a darker colour in older specimens and a more brownish one in the pupae.

In one case of such disease we detected and removed from the fibers of the thoracic muscles of apparently still unaffected and normally working bees two eggs up to 1.2 mm in length and to 1 mm in width. One of them was very young, in the other the incipient formation of mouth parts of the larva was discernible.

From the larvae found in a sample of bees taken from the most badly affected colonies of the same apiary we succeeded in 1937 to obtain a few specimens of flies. The observations made on this occasion enabled us to ascertain that the duration of the larval stage of the fly under test was 8—11 days, and that of the nymphal—12—18 days. The larvae and pupae removed from the thorax of the diseased bees, as well as the hatched flies themselves were sent by us for identification to the Zoological Institute of the Academy

of Sciences of the USSR to Prof. A. A. Stackelberg, who placed them in the group of *Metapiinae*, fam. *Sarcophaginae*.

Later on B. B. Rodendorff of the Paleontological Institute of the Academy of Sciences of the USSR determined the flies as belonging to «*Senotainia*» *tricuspis* Meig., fam. *Sarcophaginae*.

Our attempts to produce an imago in diseased bees in 1938 proved a failure. However, the larvae and pupae obtained on that occasion were determined by B. B. Rodendorff as belonging to the group *Senotainae-Metapiinae* fam. *Sarcophaginae*.

Thus, as a result of all of our investigations it was firmly established that in a number of cases heavy losses of bees occurring in the Ukrainian SSR in the summer time are caused by larvae of flies of the group *Senotainae Metapiinae*, fam. *Sarcophaginae*, living in their thorax. In one case the flies hatched from the larvae which had produced the disease, proved to be *Senotainia tricuspis* Meig., whose biological peculiarities have been hitherto unknown, and it was considered a common «wild» species of flies.

Whether it is *Senotainia tricuspis* which is producing the disease in all similar cases, or there are other species of the group *Metapiinae-Senotainae* causing them, will be seen further.

Such diseases are very widely spread in the Ukrainian SSR and evidently throughout the entire USSR. The actual damage caused by them to apiculture is not always evaluated since the death of majority of infected bees occurs beyond the field of the apiarist's observation. The apiarists take record but of the most typical cases of heavy losses of bees occurring on the territory of the apiaries. The latter circumstance is usually due either to more severe attacks, or, more frequently to the dying bees being prevented from leaving the apiary owing to rainy weather or other causes, keeping the bees confined to the hives.

The fact that more frequent cases of the above diseases causing heavy loss of bees, began to be recorded but in recent years, proves that larvae of these flies are parasitic likewise upon other species of *Hymenoptera*, but the latter, for some season unknown, ceased to play the part of the principal host, and the parasite being compelled to look for another host, happened to chose the bees. It may be here suggested that this process of changing the host involved the process of the dwindling of many species of *Hymenoptera*, like, for instance, bumble-bees and others.

It is difficult to explain the fact of occurrence in the thorax of bees of eggs of *Senotainia tricuspis* whose ovipositor is not chitinous, and hence unable to pierce the chitinuous cover of the bee's thorax.

The relation between the disease and the visiting by bees of *Thymus serpillum* pointed out by apiarists may be, evidently, accounted for by that the incovenient sandy soil where *Thymus serpillum* is growing is at the same time the station for the given species of flies.

Ukrainian Institute
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ZOOLOGY

WARM WATER *GADIDAE* IN THE BARENTZ SEA

By G. W. BOLDOVSKY

(Communicated by S. A. Zernov, Member of the Academy, 21. IV. 1939)

In the present article some data are given as to the presence of warm water *Gadidae* in the Barentz Sea. During the cruise in March-April 1938 to the west regions of the Barentz Sea on board trawler No. 48 «Sevgosrybtrest» I collected data concerning small *Gadidae*. Some of these proved to be of interest owing to which it was decided to publish them.

I. *Gadus esmarki* Nilss. All specimens of this type were caught by a net made of silk gauze fixed to the upper part of a bottom herring trawl. The specimens were discovered in the following samples:

1) March 28, 1938, 71°00′ N, 34°00′ E; depth of sea at the station 190 m, 1 specimen, L=98 mm.

2) April 8, 1938, 72°08′ N, 27°25′ E; depth of sea 230 m, 2 specimens, L=100 mm.

3) April 12, 1938, 71°23′ N, 30°32′ E; depth of sea 300 m, 1 specimen, L=130 mm.

This fish is very common for the North Sea and for parts of the Norwegian Sea (4), but this circumstance was discovered but lately, after small noose nets were introduced into practice. Up to this moment *G. esmarki* was regarded as a rare specimen in the sea basin mentioned above.

So far *G. esmarki* has not been discovered in the south part of the Barentz Sea, although ichtyological investigations have been continued here for scores of years.

Examining the map of places where this small fish was caught (figure), it is easy to note that all of them are living in the zone of immediate action of the Nordcape current. It stands to reason that *G. esmarki* penetrates to the south part of the Barentz Sea from the west by this way and that his migration is mostly due to the general increase of sea water temperature that took place during the last years.

II. *Gadus poutassou* Risso. This species of the codfish family, mostly the young specimens 5—15 cm long (the mature specimens are 35—40 cm long), was caught by us mainly at the Nordkin and Nordcape banks and, in smaller quantities, at the Finmark and south west slope of the Mourman banks.

It was first discovered among the fish caugth at one cast of the bottom herring trawl, viz., on the 10th of April (72°08′ N, 27°15′ E). At the same day about 100 kg of this fish were caught (71°57′ N, 26°00′ E). On the 11th of April, not far away from the Nordcape (71°28′ N and 25°50′ E) there were caught 30 kg of small and 3 large specimens of *G. poutassou*; the latter

ones were in the average about 35 cm long. On the 12th of April at the Nordkin bank (71°28′ N and 30°15′ E) a few dozens of these fine silver glittering fish were caught again, 25 specimens of which were dissected in order to analyze the food devoured by them.

It was discovered that in 4 of them the stomachs were quite empty, while in 2 the stomachs contained but entirely digested food, which made it impossible to judge of its composition even approximately. The stomachs of the last 19 specimens were to a different degree filled with *Euphausiidae*.

Moving from the Nordkin bank to the south-east, the last specimens of the codfish type described besides the Finmark bank (70°59′ N and 31°24′ E) have been met with on the south west slope of the Mourman bank (70°37′ N and 34°10′ E).

Map of occurrence of *Gadidae*. Symbols: 1—spot of catch of *Gadus esmarki* Nilss. □2— spot of catch of *G. poutassou* Risso in January —February 1938. 3— spots of catch of *G. poutassou* Risso in April 1938.

On the foregoing February-March cruise of the trawler No. 48 to the Mourman bank, young *G. poutassou* have been met with in many places and in more considerable quantities than it was in our case. It should be emphasized that this region was thoroughly searched during both cruises and yet during our cruise we have but once discovered in this region separate specimens of *G. poutassou*, whereas in the foregoing cruise we met it 5 times; on February 11 (71°13′ N and 33°40′ E) there were caught 20 kg and on the same day (70°30′ N and 34°40′ E) 100—150 specimens again.

Among the materials collected by the trawler No. 34 in January 1938 (69°42′ N and 40°08′ E) one specimen of *G. poutassou* was as long as 12.7 cm.

In the literature there are known the following data concerning the distribution of this species in the Barentz Sea. According to Prof. N. M. Knipowitch ([5]) *G. poutassou* is not met with east off the Nordcape. E. Ehrenbaum ([4]) classes the *G. poutassou* as a boreal species of the codfish family spread in the Barentz Sea as far as to the Finmark. In accordance with the materials collected by the Sea Bottom Fish Laboratory of the Knipowitch's Polar

Scientific Institute of Marine Fisheries and Oceanography for 1934—37, young *G. poutassou* was occasionally caught in small quantities by codfish trawls among the so-called «overcatch», especially in the western regions. Large specimens of these fishes were caught more rarely. Young specimens were found in codfish stomachs, but in small quantities, too. It is quite possible that the large catches of this fish described above were due to the use of herring trawls, with small meshes. However, from the above materials we may conclude that this fish began for the last years to appear in the west parts of the Barentz Sea in considerable quantities. Evidently, taking advantage of the Nordcape currents, *G. poutassou* penetrates, though in smaller quantities, as far east as, say, to 40° E. The utmost spread to the east seems to take place during the period of the hydrological summer. After winter colds set in, *G. poutassou* migrates to the west as all the fishes of boreal origin do in the Barentz Sea.

The occurrence of large quantities of this species in the south part of the Barentz Sea may bring about some changes in the system of feeding chains prevailing here at the present time. First of all there appears a new and evidently important consumer of the feeding plankton, chiefly of the *Euphausiidae*. In this case probably *G. poutassou*, as all fishes of the codfish family, does not lower its feeding to the minimum in the winter time. Therefore the *G. poutassou* must consume the winter stock of plankton diminishing by this way its eventual summer abundance. In other words, there appears an important rival to the plankton consuming fishes, including the herring.

On the other hand, this type of the codfish family is known to be devoured by the cod itself and by some other consumers of small fishes. Thus, the appearance of the *G. poutassou* in the Barentz Sea increases the feeding stock of these fishes.

In a work recently published by L. S. Berg ([2]) numerous cases are reported of boreal types of sea animals, mainly fishes, penetrating considerably further into the regions of the northern seas than it was previously known. Berg pointed out that expansion of the area of these species is accompanied with their numerical growth in those parts of northern seas where they were rare before. And contrariwise, many of the northern species become more numerous at the southern borders of their habitats. Prof. L. S. Berg explained these phenomena by the general increase of temperature of the earth, observed for the last 50—70 years and due to the intensification of the sun's activity.

The same question was discussed by S. W. Awerintzeff([1]) in his article. I have also reported([3]) a number of facts of penetration of warm water *Euphausiidae* (*Crustacea*) in the Barentz Sea during the last years, and of changes in their distribution.

The presence of warm water species of *Gadidae* in the South part of the Barentz Sea is to be regarded essentially as a result of the climate getting warmer.

Knipowitch Polar Scientific Institute
of Marine Fisheries and Oceanography.

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PALEONTOLOGY

DEVELOPMENT OF THE FAMILY *METALEGOCERATIDAE* PLUMMER ET SCOTT

By V. E. RUZHENZOV

(Communicated by A. A. Borissiak, Member of the Academy, 27. V. 1939)

This family was isolated in 1937 by Plummer and Scott (²). It includes ammonites widespread in the Carboniferous and Permian deposits of many countries. In this country they frequently occur in corresponding deposit along the western slope of the Urals. A study of the Ural collections permits of drawing certain conclusions as to the development of the family *Metalegoceratidae*, but before proceeding to these conclusions, let us critically analyze same of the views advanced by Plummer and Scott.

The American authors assume that the development of this family proceeded in the direction *Cravenoceras→Glaphyrites→Metalegoceras*. The ontogenetic study of representatives of the genera *Glaphyrites* and *Metalegoceras* furnishes no ground for regarding the first genus as ancestral to the second one, since their suture lines and shells differ from one another at very early stages of development. The main difference lies in the first lateral lobe being far less strongly developed in *Metalegoceras* than in *Glaphyrites* and always much shorter than the siphonal lobe. In this respect complete similarity to *Metalegoceras* is displayed by representatives of the genus *Eoasianites*. And it is for this reason that the latter should be recognized as the ancestor of the former. Besides, the study of the ontogeny shows that the genus *Eothinites* too springs from *Eoasianites*. Hence the development of the family *Metalegoceratidae* proceeded at least in two directions.

Eoasianites → *Metalegoceras*
Eoasianites → *Eothinites*

Let us consider the distribution and range of each of the above genera.

1. Plummer and Scott have isolated the genus *Trochiloceras*, which was referred by them to the family *Neoicoceratidae*. This genus was established by the authors on the basis of rather young shells (D=6.00 and 7.17 mm). These shells differ neither in general shape nor outline of the suture from early volutions of *Eoasinites* which is classed by the same authors among the family *Gastrioceratidae*. It seems to us that there are grounds to place the name *Trochilioceras* in the synonymy, while both genera referred to two families should be united under one name of *Eosianites*. From what we know, this genus persisted throughout the Upper Carboniferous and Sakmarian times.

2. Plummer and Scott stand on that *Asianites* is a separate genus which they consider as belonging to the family *Gastrioceratides*. We see no evidence

which would bear out this contention. The name *Asianites* is undoubtedly a synonym of *Metalegoceras*. The two genera assigned by the American authors to two families, should be placed under one denomination. The genus *Metalegoceras* arose in the Sakmarian time and persisted throughout the entire Artinskian period.

3. In 1933 two genera were separated by me, *Eothinites* and *Riphaeites* (1). The study of extensive material collected later on has shown, however, that the genotypes of these two genera, *Eothinites kargalensis* Ruzh. and the *Riphaeites uralensis* Ruzh., are closely related forms, and of course belong to the same genus. Consequently, the name *Riphaeites*, being used the second, is to be included into the synonymy. Plummer and Scott refer the genus *Eothinites* to the family *Metalegoceratidae*, while *Riphaeites* is considered by them as belonging to the family *Brannerocerati dae*. The conclusions of the American authors in regard to the genus *Riphaeites* fail to be supported by examination of the data in hand. *Eothinites* was widely distributed in the Artinskian stage; it was also met in synchronous deposits of Timor and Texas.

Fig. 1. *a—Eoasianites hartmannae* Ruzh., Zhaxy-Cargala river, Sakmarian stage; *b—Metalegoceras evolutum* Han., Jil-tau mountain, Artinskian stage; *c—Eothinites uralensis* Ruzh., Jil-tau m., Artinskian stage; *d—Glaphyrites* sp. det., Sakmara river, Upper Carbon. (×2.7).

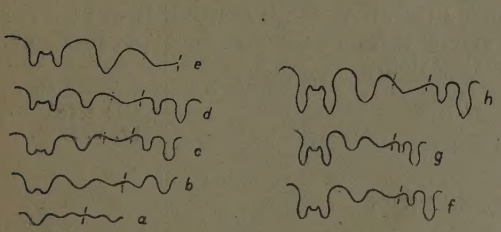

Fig. 2. *a—e—Glaphyrites* sp. d., Ural rirer, Upper Carbon.; *a*—at width (W)=0.6 mm (×17), *b*—at W=1.1 mm (×17), *c*—at=2.7 mm (×7), *d*—at W=4.7 mm (×4), *e*—at W=7.5 (×3.3); *f—h—Eoasianites hartmannae* Ruzh., Jil-tau m., Sakmarian stage, *f*—at W=1.7 mm (×8), *g*—at W=3.2 mm (×4), *h*—at W=5.3 mm (×3.3).

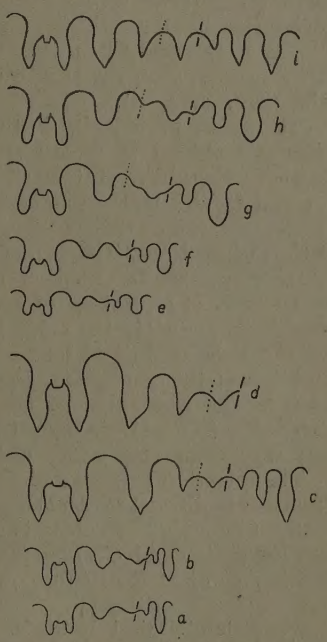

Fig. 3. *a—d—Eothinites uralensis* Ruzh.; *a*, *b*—Jil-tau m., *c*, *d*—Aktasty r., Artinskian stage; *a*—at W=1.7 mm (×7), *b*—at III= 3.2 mm (×4), *c*—at W=6.6 mm (×3), *d*—at W=8.8 mm (×3); *e—i—Metalegoceras evolutum* Han., Jil-tau m., Artinskian stage; *e*—at W=1.4 mm (×8), *f*—at W= 1.9 mm (×8), *g*—at W=2.7 mm (×8), *h*—at III=4.0 mm (×7), *i*—at W=9.2 mm (×3.3).

Now let us proceed to the data in support of the phylogenetic relations which we suggest for the family *Metalegoceratidae*.

In Fig. 1 are shown transverse sections of juvenile shells *Eoasianites hartmannae* Ruzh., *Metalegoceras evolutum* Han., *Eothinites uralensis* Ruzh. and *Glaphyrites* sp. det. Typical of the former three is the wholly

evolute condition of the early whorls. In the course of subsequent ontogenesis the curvature in representatives of the genus *Metalegoceras* expands mainly broadwise (especially in forms such as *M. sogurense* Ruzh.). In members of the genus *Eothinites*, beginning from about the 7th whorl, a particularly intense upward growth of the curvature takes place. The above figure confirms our viewpoint as to the development of the family we are concerned with. There is much less ground to consider *Glaphyrites* as the ancestral genus, its early volutions being wider and more involute in comparison to *Metalegoceras*, especially to *Eothinites*.

Fig. 2 shows suture lines in *Glaphyrites* sp. det. and *Eosinites hartmannae* Ruzh. At its early stage of development the suture line in the genus *Eosianites* has one important feature which attracts attention (Fig. 2, *f*, *g*): its first lateral lobe is very feebly developed as compared to the deep siphonal lobe. This character persists in all members of the genus which occur in the Upper Carboniferous stage*. In representatives of the genus *Glaphyrites* the siphonal lobe is appreciably less deep than in the foregoing case, and there is little difference between the length of the first lateral lobe and that of the siphonal lobe (Fig. 2, *c*, *d*).

The above peculiarity in the outline of the suture of an adolescent *Eosianites* is retained in members of the genus *Metalegoceras* and *Eothinites*. To prove the above statement it is sufficient to compare Fig. 2, *f* with Fig. 3, *a* and *e*, *f*. Thus, the kinship between the three genera, as shown above from the comparison of their adolescent shells, finds full support in the ontogeny of the suture lines. The genus *Glaphyrites* cannot be recognized as ancestral to *Metalegoceras* from this standpoint either.

The way of formation of characters, as far as the suture line alone is concerned, was exactly the same in both *Metalegoceras* and *Eothinites*. In both instances the umbilical lobe becomes tripartite, thus forming three independent lobes: the umbilical, the second external lateral and second internal lateral. The formation of the remaining characters of *Metalegoceras* and *Eothinites* (general configuration of the shell, sculpture) proceeds in a different way from very early ontogenetic stages.

The question arises as to what family the genus *Glaphyrites*, referred by Plummer and Scott to *Metalegoceratidae*, does really belong. It would be permitted to continue to class it among the above family only if it was proved that *Eoasinites* and *Glaphyrites* originate from a common ancestor. However, this is an object for further investigation.

Paleontological Institute.
Academy of Sciences of the USSR.
Moscow.

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* The same peculiarity is observable in *Trochilioceras tenuosum* P. et S.

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